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MOTOR VEHICLE SAMPLING EXPERIMENT

FINAL REPORT

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Prepared for

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ABSTRACT

In order to determine the changes in air quality along major freeways resulting from the introduction of catalysts or other control devices on automobiles to reduce the emissions of carbon monoxide and hydrocarbons, measurements of the air quality were performed just before catalyst equipped vehicles were introduced. Data were collected for 12 days in August and September 1974 on either side of the San Diego Freeway in Los Angeles just south of Wilshire Boulevard. Measurements included meteorological conditions, trace gas concentrations, aerosol number concentrations and size distributions, and twohour filter samples which were analyzed for a number of elements and species. The data have been edited and collected into a data base of 10 minute, onehour, and two-hour averages. All known limitations in the data are carefully Pollutant concentration differences due to the traffic are tabulated, as well as concentration differences divided by the $NO_{\rm X}$ concentration difference. Reduced nitrogen and sulfur species were observed, as well as a volatile sulfur component in the aerosol. A new method of reducing electrical analyzer data was developed.

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We also wish to acknowledge the guidance and cooperation of Jack Suder and other members of the ARB staff in the conduct of this program, and the cooperation of the Air and Industrial Hygiene Laboratory and the Naval Weapons Center, China Lake, California, who were also contractors.



2.0 CONCLUSIONS

The data bank documenting the air quality along a major Los Angeles freeway just before the introduction of catalyst equipped automobiles has been collected, edited, and compiled on magnetic tape. No new air quality problems were discovered in this study, and more recent studies reviewed in this report indicate that sulfate concentrations due to catalyst equipped cars are now appreciably less than projected at the time this study was initiated. The limitations of the data bank collected in this study are described in the report.



3.0 RECOMMENDATIONS

No recommendations for further Air Resources Board actions have been developed from the data obtained in this study. It appears that the sulfate emissions from vehicles are low enough that no action related to them is required at this time.



4.0 INTRODUCTION

This Motor Vehicle Sampling Experiment is the first phase of a California Air Resources Board (ARB) program to measure the changes in near roadway ambient air quality resulting from the use of oxidative catalysts on automobile exhaust systems. The field measurements were made in August and early September 1974, just as the first catalyst equipped vehicles were being sold. The continuing work in this program is being conducted by the ARB staff from the El Monte Laboratories (Bockian, et al. 1977).

4.1 BACKGROUND

In order to comply with the provisions of the 1970 Clean Air Act, motor vehicle manufacturers began using catalystic converters in the exhaust systems of most automobiles beginning with the 1975 model year. The catalysts were primarily designed to control the hydrocarbon and carbon monoxide emissions, but had the unintended property of oxidizing the sulfur in the fuel to sulfur trioxide. On entering the atmosphere, sulfur trioxide is very rapidly converted into a fine mist of sulfuric acid.

The discovery of the emission of sulfuric acid and the early work on the problem has been reviewed by Pierson, Hammerle, and Kummer (1974) and by Bradow and Moran (1975). It was observed in 1971 that catalyst equipped vehicles burning non-leaded fuel had increased particulate emissions (Moran, Manary, Fay, and Baldwin, 1971), but it was not until early 1973 that it became generally known that these emissions were largely sulfuric acid. Since that time, a great deal of work has been done on the problem.

It appears that the processes which lead to the sulfate emissions are rather complex, and that many factors play a role. As a result, the determination of emission factors for catalyst equipped automobiles is still in progress. At the present time, it is clear that at least the following factors are important in determining the sulfate emission rate from a catalyst equipped vehicle:



- Fuel sulfur concentration. It is a good approximation that the sulfate emission rate is proportional to the concentration of sulfur in the fuel.
- Catalyst temperature. At the mid-range and upper catalyst temperatures, thermodynamic equilibrium is established between sulfur dioxide, oxygen, and sulfur trioxide in the catalyst. At equilibrium, higher temperatures give lower conversions to sulfate. At low temperatures, the oxidation of SO₂ is rate limited, and lower temperatures give lower conversions.
- Excess oxygen concentration. It follows from the fact that equilibrium is often achieved, that more oxygen in the exhaust leads to greater conversion of sulfur dioxide to sulfate. Therefore, California cars equipped with air pumps typically have higher sulfate emissions than 49-state cars.
- Sulfate storage. As much as 3% of the alumina catalyst support can be converted to aluminum sulfate, with the result that large amounts of sulfur can be stored in the catalyst unit. Therefore, sulfate emissions depend on the previous driving history of the car. Storage tends to reduce sulfate emissions, because sulfur dioxide is not stored at all, and when stored sulfates are released, they are usually released in thermodynamic equilibrium between sulfur dioxide and sulfate. Stored sulfates can also be rapidly stripped to form SO₂ by CO, hydrogen, or olefins, which occur in the exhaust under fuel rich conditions.
- Driving mode. It is generally observed, for reasons which follow in part from the above observations, that driving at a variable speed produces lower sulfate emissions than driving steadily at the same average speed. The speed fluctuations need not be very large to observe this effect.
- Wehicle and test. Supposedly identical vehicles show wide vehicle-to-wehicle variations in the sulfate emission rate. Also, test results on the same vehicles are not as reproducible as one would like.
- Catalyst age. Recent work discussed below shows that the catalyst in consumerowned vehicles deteriorate more rapidly than those in test or certification vehicles. In addition, catalysts fortunately lose their ability to oxidize sulfur dioxide more rapidly than they lose their ability to promote the oxidation of hydrocarbons and carbon monoxide.

Perhaps the best current information on the sulfate emission rate for



catalyst equipped cars in actual use is contained in the papers by Herling \underline{et} \underline{al} . (1977) and Gibbs \underline{et} \underline{al} . (1977) presented at the February 1977 Society of Automotive Engineers meeting. The work of Herling \underline{et} \underline{al} . shows the typical great variability of the sulfate emission rate between vehicles, and also shows a decrease from a rate of 16 mg/mi at an average of 3500 mi to 7.6 mg/mi at an average of 12,500 mi for the same set of California cars. These figures are to be compared with the 37 mg/mi observed with low mileage California (air pump equipped) cars in the General Motors Sulfate Dispersion Experiment (Cadle \underline{et} \underline{al} ., 1976). If the test results of Herling \underline{et} \underline{al} . for the fleet of 100 California cars are typical, then the following conclusions can be drawn:

- It will not be necessary to wait untill all vehicles are equipped with catalysts (about 10 years) in order to reach a steady state sulfate emission rate. It will only be necessary to wait long enough for the catalysts of the 1975 vehicles to lose their ability to oxidize sulfur compounds, which may take only two or three years.
- Actual sulfate emission rates on California freeways are now and will be much lower than estimated early in 1975 when this problem was being assessed.
 (See, for example, the CARB staff report on this topic, 1975).
 Of course, sulfate emission rates in the future depend strongly on control technology decisions made by the automobile manufacturers.

Several measurement programs other than the one reported here have been undertaken to determine the concentrations of sulfate due to catalyst equipped cars which actually occur on roadways. The largest is the Los Angeles Catalyst Study sponsored by the EPA. The data from this program are obtained at four fixed sites on the San Diego Freeway in West Los Angeles, just north of the site used in this study. The measurements include the determination of the concentration of a great variety of gaseous and particulate species in addition to sulfates. In the spring of 1976, it was reported that the average afternoon increase in concentration of sulfate across the freeway measured on hi-vol samplers was $5~\mu\text{g/m}^3$ (see, for example, Criteria and Special Studies Office, HERL, EPA, 1977), but it was widely felt that some of this was due to the artifact formation of sulfate on the filters from sulfur dioxide. At the April 1977 meeting at Research Triangle Park in which the results of this program to date were sum-



marized, it was reported that when the sulfate data from all methods are combined, the best estimate of the across freeway sulfate difference is about $0.5~\mu g/m^3$ (Rodes and Evans, 1977).

A significant turn in the attitude of the EPA toward the catalyst sulfate problem resulted from an analysis of Papetti and Horowitz (1975). They constructed a statistical model to determine the distribution of exposures to sulfuric acid that might be expected by commuters in Los Angeles. It was found that the upper bound exposures which had been estimated (for example, 290 $\mu g/m^3$ in the analysis of Papetti and Horowitz) were extremely improbable. This highest concentration occurred with only a probability of 6 \times 10⁻⁷ in the Papetti and Horowitz results. Furthermore, the concentration which occurred with 99% probability in their upper limit estimate was 12 μ g/m³, and the median concentration was less than 2 $\mu g/m^3$. These numbers represent and upper bound, and are not large compared to sulfate concentrations due to other sources. Furthermore, they were calculated at a time when the best estimates of the emission rates were about three times higher than suggested by the work of Herling (1977). If, in addition, the degradation of the sulfate emission rate with increasing mileage is taken into account, it would be reasonable to reduce the concentration distribution estimates of Papetti and Horowitz by a factor of six or more. Then the 99% probability concentration becomes $2 \mu g/m^3$ or less. The analysis of Papetti and Horowitz was one of the significant pieces of information considered when the EPA decided not to promulgate a sulfate standard for vehicles. The conclusions to be drawn from the analysis become even more clear now that the estimates of actual emission rates are lower.

At about the same time, the General Motors Corporation sponsored an experiment at the Milford Proving Ground (Cadle et al., 1976, 1977). The EPA was invited to participate in this experiment (Stevens et al., 1976, Wilson et al., 1977). It was found that low mileage, air pump equipped California cars had an average sulfate emission rate of 37 mg/mi, when driven at steady speed on the test track, and that the emitted sulfates initially were in the nuclei mode particle size range. In addition, it was found that the maximum sulfate concentrations near the roadway were significantly lower than predicted by the EPA HIWAY model under stagnant conditions, and that the sulfate concentrations fell off rapidly with increasing distance from the roadway. These observations led to the conclusion that the population primarily at risk is the vehicle



occupants on the freeway.

To directly measure the exposure of commuters to sulfuric acid and related sulfates due to catalyst equipped cars, the EPA has initiated a program which is still continuing in Los Angeles. In the first phase of the work, participants from Caltech, the University of Minnesota, Washington University, and the Air Monitoring Center took measurements for two weeks in the fall of 1976 (Richards, 1977). The in-roadway sulfate levels found in this study were much lower than expected. On most days, they were below the limit of detection, which was primarily determined by the high and variable background sulfate concentrations. On the day when the excess concentration of sulfate on the roadway was most clearly seen, its concentration was estimated to be 0.6 $\mu g/m^3$. Dr. W. R. Pierson of Ford Motor Company has pointed out that the sulfate concentrations observed in this study are low compared to the roadway sulfur dioxide concentrations, even when the lowest measured sulfate formation rates in catalysts and the emissions of diesels are considered in the data interpretation. Therefore, there is some question that the actual roadway sulfate concentrations are as low as reported by this study. However, it does seem safe to conclude that the sulfate concentrations on freeways due to catalyst equipped cars in October 1976 did not exceed 2 μ g/m³ when averaged over the filter collection times, which were typically near one-half hour. Therefore, it appears that sulfates from catalyst equipped cars are not now a problem on California roadways, and are not likely to become a problem until vehicle manufacturers change to different control devices. Such changes are probable, because it appears that present vehicle are not meeting the standards (Herling et al., 1977). To obtain better confidence through better data that the sulfate emissions from catalyst cars are indeed not a source of concern, the EPA programs to make roadside and in-roadway measurements are continuing.

Sulfates are not the only species emitted from cars equipped with control devices. The emission of noble metals, nickel carbonyl from catalysts which contain nickel, hydrogen cynanide from three-way catalysts, and manganese from the use of MMT as a fuel additive have all been sources of concern. Therefore, this study of the concentrations near a freeway shortly before the first cars with catalysts came into use included the measurement of the concentration of a number of metals and other gaseous and particulate species.



4.2 OBJECTIVE

The objective of the study reported here is to characterize the effect of a major freeway on air quality near the roadway before the introduction of the catalytic converters in exhaust systems. The study emphasized the determination of the physical properties and chemical composition of the emitted aerosols. All valid data are recorded in an edited magnetic tape data bank, and are available for future reference.

4.3 ORGANIZATION

The Motor Vehicle Sampling Experiment was carried out by three cooperating contractors under three separate contracts with the California Air Resources Board. This section of the report describes the organization of the program and the responsibilities and major tasks of each of the contractors. The study was under the direction of Drs. Albert Bockian and Jack Suder of the Research Section of the ARB.

The Rockwell International portion of this study was initiated by Dr. G. M. Hidy and the Science Center staff, and the program was transferred to the Air Monitoring Center (AMC) when that organization was formed from the Science Center. The field program was conducted by H. H. Wang. The responsibilities of the AMC were:

- Site selection and preparation.
- Logistics and coordination of the sampling episodes.
- Calibration of the sampling flow rate of the "Q" automatic sequential filter samplers.
- Calibration of the aerosol instrumentation in the ARB mobile laboratory, the Royco OPC in the NWC laboratory, and assistance in the calibration of the CNC and EAA in the NWC mobile laboratory.
- Operation of all equipment and systems in the ARB mobile laboratory on the east side of the freeway except for the filter samplers and instruments measuring concentrations of gases.
- Reduction and tabulation on a magnetic tape of all data from the ARB mobile laboratory.



- The analysis and interpretation of the data from all contractors.
- The preparation of a final report.

The work by the Air and Industrial Hygiene Laboratory, California Department of Health (AIHL) was carried out under the direction of Dr. Bruce Appel. The responsibilities of AIHL were:

- Calibration of all instruments measuring gas concentrations.
- Calibration of all flow rates on filter samplers, except the "Q" samplers.
- Operation of all filter samplers on the west side of the freeway (at the ARB mobile laboratory).
- Providing pre-weighed filters for all filter samplers, returning the filters to the laboratory, analyzing them, and coordinating the analyses to be performed by other laboratories (Lawrence Berkeley Laboratory and University of California at Davis).
- Preparing a data tape containing validated results from all filter analyses.
- Preparation of a final report.

The Technology Utilization Office, Naval Weapons Center, China Lake, California (NWC) provided and operated a mobile laboratory on the east side of the freeway. The NWC work was directed by Paul Owens, and their responsibilities were:

- Calibration of nephelometer and some other aerosol instruments in the NWC mobile laboratory (see AMC responsibilities).
- Operation of all instruments and filter samplers on the west side of the freeway.
- Preparation of a magnetic tape of validated data from the aerosol, gas measuring and meteorological instruments on the west side of the freeway.

The AIHL transmitted its instrument calibration data directly to the operator of each mobile laboratory, so those calibrations could be used when processing the magnetic tapes to produce the final data tapes. Both AIHL and NWC sent their final data tapes to the AMC so that the data base could be analyzed and interpreted as a whole. The AIHL final report has been prepared and approved by the Research Screening Committee of the ARB (Appel and Wesolowski, 1975).



5.0 PREPARATIONS AND OPERATIONS

This section of the report discusses the selection of the site for the field measurements, and describes the procedures used for the calibration of the instruments, the field operations, and the processing of the data.

5.1 SITE SELECTION

The sampling strategy was to locate the two mobile laboratories on opposite sides of a major freeway so that concentration differences could be measured. By subtracting the data obtained at the upwind location from those measured downwind, it was possible to determine the contribution of the freeway traffic to the observed pollutant concentrations at the downwind location.

The criteria used in the selection of the site for the field measurements were as follows:

- The wind direction must be approximately perpendicular to the freeway much of the day.
- The traffic density must be high, so that measurable differences in pollutant concentrations can be obtained for as many atmospheric components as possible.
- Traffic counting equipment must be available.
- The traffic pattern should vary during the sampling period so that data can be obtained for various engine operating conditions.
- The sites should be relatively free of local traffic, so that emissions from vehicles other than those on the freeway will not appreciably influence the concentration differences.
- The local area and the region from which the prevailing winds come should be free of major stationary sources.
- The sampling site should not be at a major cut or fill, and should be some distance from large buildings or other obstructions.
- The site should offer some measure of security from theft and vandalism.

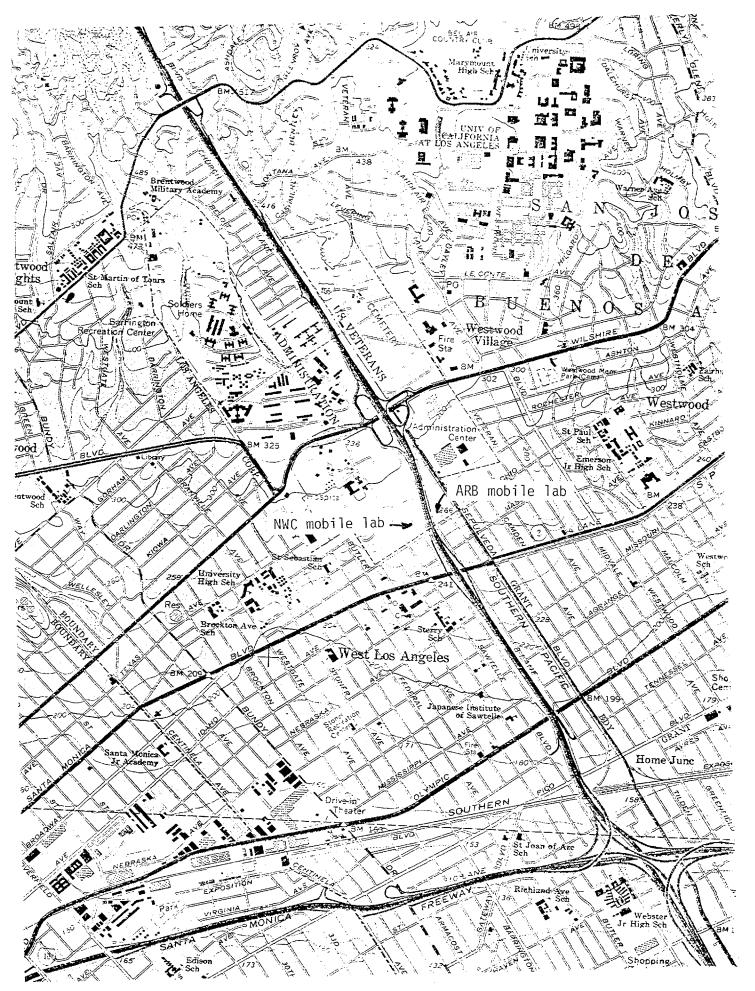


Figure 5-1. Map Showing the Locations of the Mobile Laboratories



The sampling site selected was the Veteran's Administration grounds in West Los Angeles on the San Diego Freeway (Interstate 405), and is shown in Figure $5\cdot 1$. This site satisfies all of the above criteria, except that the freeway is on a fill about 5 m (15 ft) high. There are some trees in the area, but they were not dense enough to significantly affect the data.

The ARB mobile laboratory was on the east side of the freeway, which is the downwind side much of the day, as close to the roadway as possible. The sample intake for this laboratory was 6 m (20 ft) above the ground, and hence was at about the same elevation as the roadway surface. The sample intake and filter samplers were about 10 m (30 ft) from the near edge of the freeway pavement. The instrumentation is listed in Table 5-1.

The NMC mobile laboratory was on the east side of the freeway about 60 m (200 ft) from the edge of the pavement. This distance was chosen to minimize the impact of the freeway on the NWC data when the winds were generally from the west, but were light and variable. The instrumentation in the NWC mobile laboratory is listed in Table 5-2.

The San Diego Freeway is one of the most heavily traveled major arterials connecting the San Fernando Valley population to the north with the Santa Monica Freeway and the business and industrial facilities in Torrance, El Segundo, Culver City, Hawthorne and Long Beach to the south. The diurnal pattern for vehicular movement on the San Diego freeway is primarily high density at high speeds during much of the day. During the rush hours, from about 0730 hour to about 0830 and again from about 1600 hour to about 1730 hour, traffic is particularly congested and speeds are reduced. The local traffic is heaviest on Wilshire Blvd. to the north, and Santa Monica Blvd. and Santa Monica freeway to the south. The westerly wind, when established in the latter part of the sampling day, is quite free of spurious contributions from local traffic.

Typical wind speed and direction data for this location are shown in the latter portion of Appendix A. As the onshore breeze develops, the upwind samples become characterized by the relatively clean ocean air.



Table 5-1 INSTRUMENTATION FOR THE ARB MOBILE LABORATORY

| Instrument | Parameter Measured | Manufacturer | Model No. |
|--|---|-------------------------------|------------|
| Aerosols Condensation Nuclei Counter (CNC) | Total Aerosol Number Concentrations | Environment/One | Rich 100 |
| Optical Particle Counter (OPC) | Aerosol Size Distribution (0.3 to 5 μm diameter range) | Royco | 220 |
| Electrical Mobility Analyzer (EAA) | Aerosol Size Distribu- tion (0.01 to 0.4 μm diameter range) | Thermo-Systems, Inc. | 3000 |
| High-Volume Sampler (2) | | | |
| Integrating Nephelometer | Total Aerosol Light Scattering | Meteorology Research, Inc. | 1550 |
| 2-stage hi-vol sampler | Respirable Particulates (≲3.5 µm diameter) | | |
| Automatic Sequential Sampler | Total Particulates | Rockwell International | |
| Meteorology Meteorological Measurement System | Wind Speed and Direction | Meteorology Research, Inc. | 1074 |
| Thermometers | Temperature | Rosemount | 412R |
| Spectral Pyranometer | Total Radiation | Eppley Laboratory, Inc. | 2(1154 F3) |
| Ultra-Violet Radiometer | Ultra-Violet Radiation | Eppley Laboratory, Inc. | 2(11692) |
| Humeter | Relative Humidity | Phys-Chem Corp. | |

Table 5-1 (Continued)

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| <u>Instrument</u> | Parameter Measured | Manufacturer | Model No. |
|--|---|----------------------------------|-----------|
| Gaseous Pollutants | <u>.</u> | | |
| Chromatograph | Total HC, Non-Methane HC, C2H4, C2H2, and Carbon Monoxide | Beckman | 6800 |
| NO-NO _X Analyzer (Chemilumines- cent) | Nitric Oxide Nitrogen Oxides | Bendix | 8101B |
| SO ₂ Analyzer (GC-flame photometric) | Sulfur Dioxide Hydrogen Sulfide | Varian | 1440 |
| Ozone Analyzer (Chemilumines- cent) | 0zone | REM | 612 |
| Data Acquisition | | | |
| Computer | | Digital Equipment Corporation | PDP-8/E |
| Software | | Rockwell International | |



Table 5-2

INSTRUMENTATION FOR THE NAVAL WEAPONS CENTER MOBILE LABORATORY

| Instrument | Parameter Measured | Manufacturer | Model No. | | | |
|--|---|------------------------------|-----------|--|--|--|
| <u>Aerosols</u> | | | | | | |
| Condensation Nuclei Counter (CNC) | Total Aerosol Number Concentration | Environment/One | Rich 100 | | | |
| Optical Particle Counter (OPC) | Aerosol Size Distribution (0.3 to 5 μm diameter range) | Royco | 220 | | | |
| Electrical Mobility Analyzer (EAA) | Aerosol Size Distribution (0.03 to 0.7 μm diameter range) | Thermo-Systems, Inc. | 3030 | | | |
| Integrating Nephelometer | Total Light Scattering | Meterology Research, Inc. | | | | |
| 2-stage hi-vol sampler | Respirable Particulates (\lesssim 3.5 μm diameter) | | | | | |
| Automatic Sequential Sampler | Total Particulates | Rockwell International | | | | |
| Meteorology | | | | | | |
| Meteorological Measurement System | Wind Speed and Direction | | | | | |
| Thermometers (Mercury) | Temperature | | | | | |



Table 5-2 (Continued)

Atomics International Division
Air Monitoring Center

| Instrument | Parameter Measured | Manufacturer | Model No. |
|--|-----------------------------------|--------------|-----------|
| Gaseous Pollutants | | | |
| NO-NO _X Analyzer (Chemilumines- cent) | Nitric Oxide Nitrogen Oxides | REM | |
| Sulfur Gas Analyzer | Sulfur Dioxide | Meloy | SA 160 |
| Ozone Analyzer (Chemilumines- cent) | Ozone | REM | 612 |
| Non-Dispersive Infrared Analyzer | Carbon Monoxide Carbon Dioxide | Bendix | |
| Data Acquisition | | | |
| Data Logger | Metrodata | | |



5.2 INSTRUMENT CALIBRATION

The analyzers and the filter samplers were calibrated once at the beginning of the study and once at the end. A team from AIHL field calibrated the trace gas analyzers for both the ARB and the NWC mobile laboratories, as described below. The 47 mm filter collection system in the ARB trailer was calibrated by AIHL at the Science Center by measuring the pressure differential across an orifice. The "Q" sequential samplers were calibrated by the AMC using a dry test meter. The respirable hi-vol samplers were calibrated by AIHL at the Science Center with a hot-wire anemometer referenced to a standard orifice at AIHL.

The AMC calibrated the optical particle counters (OPC) and associated multi-channel analyzers (MCA) for both the ARB and the NWC mobile laboratories. The operators of these instruments made zero adjustments during the field program as required. The calibrations were performed using dioctylphthalate drops of known size from the Berglund-Liu vibrating orifice aerosol generator (Berglund and Liu, 1973), and by using polystyrene latex beads of known size. The data from each channel of the 250 channel MCA in the ARB laboratory and the 128 MCA in the NWC laboratory were recorded in the field. During the data analysis, the data were combined into four diameter size ranges centered about the latex bead or DOP droplet diameters.

The factory calibrations for the electrical aerosol analyzers (EAA) were used. The Model 3030 EAA in the NWC mobile laboratory was operated in the standard manner for charging conditions of Nt = 7×10^6 (ions/cm³)(sec) (Liu and Pui, 1975).

The condensation nuclei counters were calibrated by NWC and AMC personnel by comparison with the EAA. However, the CNC has a sensitivity to particles as small as 0.003 μm , while the lower size limit of the EAA is about 0.03 μm . Therefore, a Teflon bag was used to age a freeway aerosol sample sufficiently to coagulate the very fine nuclei mode aerosols, so that the size distribution of the aerosol in the bag fell within the range of both instruments. Under



these circumstances, the CNC can be calibrated by adjusting it to give the same readings as the EAA (Liu and Pui, 1974).

The CNC diluters were calibrated in a similar manner. These diluters, made from commercially available in-line filters, were required for the CNC due to the extremely high number density of nuclei mode aerosol near the freeway. A series of six diluters with varying dilution efficiencies were built and used. The diluters were calibrated by comparing the CNC readings with and without the diluter when sampling from a bag of aerosol prepared as described above.

Factory calibrations were used for all meteorological instrumentation. The trace gas analyzers were calibrated by the AIHL team. For the hydrocarbon/carbon monoxide analyzer, a cylinder of mixed methane, carbon monoxide, ethylene and acetylene in nitrogen was used as standard. For the sulfur analyzers, a sulfur dioxide permeation tube was used as reference. Since the mixed hydrocarbon/CO calibration gas and the permeation sources were carried on the ARB trailer, daily calibrations were performed for these two analyzers. The calibration gas and the permeation tube were verified at AIHL by comparison to a known standard and by observing the weight-loss rate as the permeation rate.

The oxides of nitrogen analyzers were calibrated by the AIHL team using a cylinder of nitric oxide in nitrogen as a transfer standard. The ${\rm NO_2/NO_X}$ channels were calibrated by the ${\rm As_2O_3}$ conversion of NO to ${\rm NO_2}$.

The ozone analyzers were calibrated by the standard iodine titration technique. A regulated stream of ozone from an ozone generator was first introduced to the ozone analyzers and then to a bubbler of buffered KI solution.

5.3 OPERATIONS

The actual sampling took place during four weeks in late summer just prior to the introduction of the catalyst equipped 1975 model cars. From August 14 through September 5, 1974, fourteen hours of data were collected each day, three days per week for a total of twelve sampling episodes. During each



episode, team members from each of the three laboratories were generally divided into two shifts. A typical episode on the ARB trailer began at 0500 hour with the arrival of the morning shift to prepare the instruments for the day's run. All the analyzers underwent a zero adjustment. In addition, the Beckman hydrocarbon analyzer was calibrated with the on-board cylinder of calibration gas and the Varian sulfur analyzer was calibrated with a permeation tube. A new magnetic tape was loaded and the computer data acquisition system set to a stand-by condition. After the filters were loaded into the respirable high-volume samplers and the 47 mm filter holders, the data run was ready to begin at 0600 hours.

Most instruments were interfaced with the computer data acquisition system. Analog signals from each instrument were sampled at twenty second intervals, averaged, and stored on magnetic tape (DECtape) every ten minutes. The filter samplers were manually changed every two hours. The laboratory operators continuously monitored the operation of all analyzers. Also, manual relative humidity readings were taken with the sling psychrometer at about every half hour as a verification and calibration of the electronic humidity sensor.

At 1300 hour, the afternoon shift began and the sampling day continued until 2000 hours, when the episode was terminated. The following hour was spent securing the mobile laboratories for the next episode. This sampling procedure was repeated three times a week for four weeks.

The first and the last day of each week was used to calibrate instruments, perform minor instrument maintenance and to replenish consumables used up during the week. Since the AIHL and NWC team members were traveling long distances between home and West Los Angeles, these two days also provided some relief from the intensive schedule. Table 5-3 lists the sampling episodes by date and their identification codes.

Table 5-3

IDENTIFICATION CODES FOR THE DATA

| Sampling Day | Date 1974 | Code for NWC Mobile Data (west side) | Code for ARB Mobile Data (east side) |
|-----------------|-------------|--|--|
| 1 | August 14 | NA | OA |
| 2 | August 20 | NB | ОВ |
| 3 | August 21 | NC | OC |
| 4 | August 22 | ND | OD |
| 5 | August 23 | NE | 0E |
| 6 | August 27 | NF | 0F |
| 7 | August 28 | NG | OG |
| 8 | August 29 | NH | ОН |
| 9 | August 30 | NI | OI |
| 10 | September 3 | NJ | OJ |
| 11 | September 4 | NK | 0K |
| 12 | September 5 | NL | 0L |

5.4 DATA PROCESSING

Data collected by AMC, NWC and AIHL were independently processed and reduced to three tapes. These separate tapes were then delivered to the AMC for further processing and analysis. Figure 5-2 shows a schematic flow diagram of the data processing steps. The filter chemistry data from AIHL were in the form of computer cards and an industry standard 7-track magnetic data tape.

Two data loggers were used by NWC in collecting all of the aerometric data except for those from the optical particle counter. The MCA output was punched on a teletype paper tape. Cassette tapes from the Metrodata and Gould data loggers were sent out to be copied onto industry compatible 7-track magnetic data tapes. These tapes were combined, verified, and corrected on the UNIVAC computer at the NWC facility before delivery to the AMC for analysis.

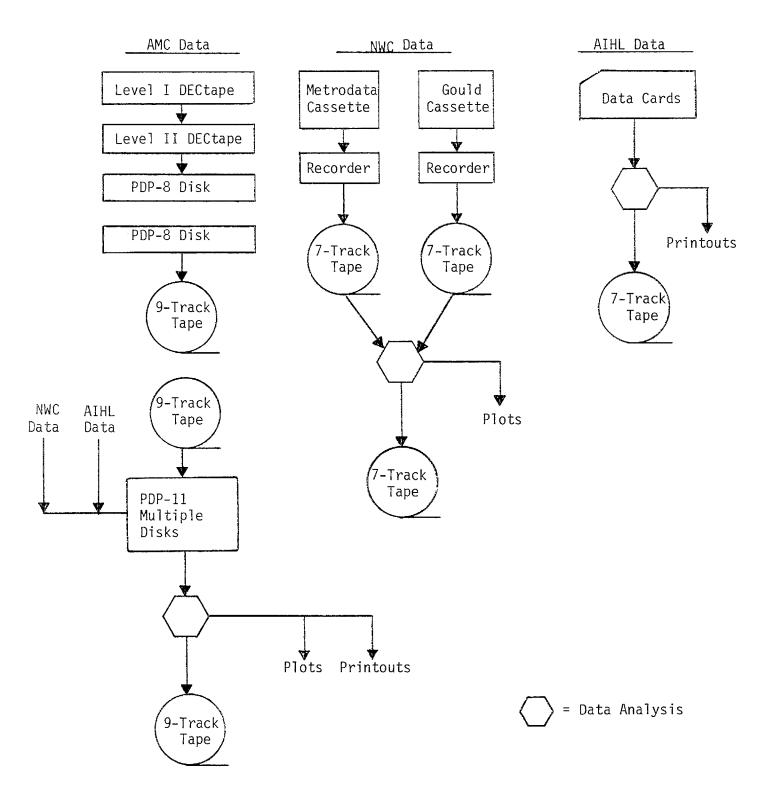


Figure 5-2. Flow Diagram of the Data Processing Steps



On the ARB/ACHEX mobile laboratory, all air chemistry data and particle size distribution information were continuously recorded on DECtapes (Digital Equipment Corporation), except for the sling psychrometer readings and the Varian sulfur dioxide data on strip charts. The DECtapes were brought back for verification and processing. Corrections, deletions and additions of manually recorded data were incorporated on the Digital Equipment computers at the Rockwell AMC facility.

An industry compatible 9-track magnetic tape was then generated, ready for further analysis. It was at this point that data from all three laboratories were compared and combined into merged files. The final "deliverables" consist of three sets of data tapes representing the data bases generated by the respective laboratories, and two merged files of one- and two-hourly averaged data. The formats for the data tapes are described in Appendix A of this report.



6.0 DISCUSSION OF THE GAS CONCENTRATION DATA

Data were obtained on both sides of the freeway for the concentrations of carbon monoxide, ozone, nitric oxide, nitrogen dioxide, and sulfur dioxide. In addition, carbon dioxide was measured on the west side of the freeway, and on the east side of the freeway gas chromatographic measurements were made of total hydrocarbons, methane, ethylene, and acetylene. The instruments used for these measurements are listed in Tables 5-1 and 5-2, and it should be noted that the same measurement technique was used on opposite sides of the freeway only for ozone and the nitrogen oxides. The data for each of these gases are discussed below.

6.1 OZONE

Ozone is the only gas which was measured by the same instrument on both sides of the freeway. Also, ozone is the only pollutant whose concentration consistently decreased between the upwind and downwind side of the freeway. This decrease was caused by the rapid reaction between the ozone and the NO emitted by the freeway traffic. On the average, the ozone concentration decreased by 0.03 ppm across the freeway during the afternoon when the sea breeze was well established.

6.2 NITROGEN OXIDES

The chemiluminescent monitors for the nitrogen oxides directly measure the concentrations of NO and of NO $_{\rm X}$, which is the sum of the concentrations of NO and NO $_{\rm 2}$. The NO $_{\rm 2}$ concentration is determined from the difference between the readings. These measurements are susceptible to interferences from other nitrogen containing gases (Winer, Peters, Smith and Pitts, 1974). In the afternoon, the average increase in the concentrations of nitrogen oxides across the freeway was 0.15 ppm for NO and 0.08 ppm for NO $_{\rm 2}$. If the reaction with ozone did not take place, the NO increase would be larger and the NO $_{\rm 2}$ increase would be smaller by the amount of ozone consumed, which was 0.03 ppm on the average.



The average difference in the NO_{X} concentration across the freeway was 0.23 ppm, and of course, this difference is not affected by the reaction with ozone. Of all the concentration differences due to the freeway traffic, the NO_{X} difference was the one which was best measured. In part, this was due to the fact that the difference was usually larger than the background concentrations. In addition, this was due to the fact that the data were recorded essentially continuously on instruments on opposite sides of the freeway which used the same measurement method. The two-hour average lead data from the filters was the next best indicator of the contribution of the freeway traffic to the measured concentration differences.

6.3 CONCENTRATION NORMALIZATION

Many factors can influence the measured concentration differences across the freeway. These include the emission rates, the meteorological conditions, and the location of the measurement sites. To remove the effect of the meteorological conditions as much as possible, the observed two-hour average concentration differences for each pollutant were divided by the average NO_X concentration difference for the same time period. To some degree, the variations in the traffic density would also be removed by this normalization. These normalized differences are primarily a measure of the ratio of the rate of emission of each pollutant to the rate of emission of nitrogen oxides per unit length of highway. A knowledge of the emission factor for nitrogen oxides then permits the calculation of the emission factor for any other pollutant for which the normalized differences have heen measured.

Several other pollutants were considered when selecting NO_{X} as the one against which all others would be compared. Carbon monoxide was eliminated from consideration because different measurement techniques were used on opposite sides of the freeway, and one of the techniques was subject to considerable statistical variation. In addition, the CO difference divided by the upwind CO concentration was not as large as was the NO_{X} difference divided by the upwind NO concentration.



The lead differences were also considered for use in the normalization, and could have been used about as well as the NO $_{\chi}$ difference. One disadvantage of the lead data is that only two-hour average information was available. Examination of the lead differences normalized by the NO $_{\chi}$ differences in Appendix B shows some variation in the relative values of these quantities, but in general they followed each other quite well.

6.4 CARBON MONOXIDE

As mentioned above, the quality of the CO data was impaired by the use of two different instruments. In addition, the data in the ARB mobile laboratory, which was usually on the downwind side, were taken by a Beckman 6800 gas chromatograph, and showed considerable statistical fluctuation. This fluctuation is believed to have arisen from the sampling procedure. The air from the sampling manifold was drawn directly through the sampling loop of the chromatograph, so that instantaneous values of the CO concentration were measured. Because of the atmospheric turbulence, the air entering the sampling manifold almost certainly contained widely fluctuating amounts of automobile exhaust, which would explain the observed fluctuations in the chromatographic readings. Because the chromatograph obtains only 12 points per hour, few enough points are included in the one and two hour averages to adequately remove these statistical fluctuations. As a result, it is believed that CO data from other studies are more useful than those from this program. Better CO data would have been very useful, because a great deal of information on CO emission factors is available.

The average difference in CO concentrations for all data taken after 1200 hr, when the sea breeze is well developed, is 2.8 ppm. Because of the fluctuations in the CO data, the normalized differences $\Delta \text{CO}/\Delta \text{NO}_{\text{X}}$ varied from -3.64 to 48.5. The average value for the normalized difference for all data taken after 1200 hrs was 14.



6.5 SULFUR DIOXIDE

The sulfur dioxide instrument in the NWC mobile laboratory apparently malfunctioned or was miscalibrated for the first seven episode days, because the data were about a factor of ten larger than expected, and ranged up to 3 ppm. Thus, reasonable $\rm SO_2$ difference data are available only for the last five days, which have codes H through L. In this case also, the data are affected by the use of different instruments on opposite sides of the freeway.

The 35 two-hour average differences for ${\rm SO}_2$ do not show a good correlation with the ${\rm NO}_{\rm X}$ differences. The ratio ${\rm NO}_{\rm X}/{\rm SO}_2$ contains seven negative values, and varies from -1.07 to 0.86. The average sulfur dioxide concentration difference across the freeway is 7 ppb. In no case out of five two-hour averages was the sulfur dioxide concentration higher at the west side of the highway when that side was downwind. Therefore, the sulfur dioxide data are best characterized by saying that the differences were below the limit of detection.

6.6 HYDROCARBONS

Data for hydrocarbon concentrations were obtained only at the ARB mobile laboratory with the Beckman 6800 Air Quality Chromatograph, and include data for total hydrocarbons, methane, ethylene, and acetylene. The background hydrocarbon concentration was quite high, with total hydrocarbon concentrations, expressed as CH₄, normally ranging between 2 and 4 ppm. The methane concentrations were also quite high, averaging about 55% of the total hydrocarbon concentration. The variation in the background hydrocarbon concentrations makes it unreliable to attempt to use the early morning wind direction reversals to assess the traffic contribution to the hydrocarbon concentrations.

The same situation exists for the ${\rm CO}_2$ data, which was obtained only at the NWC mobile laboratory. The ${\rm CO}_2$ background concentrations were normally between 300 and 400 ppm.



6.7 DIURNAL PROFILES OF CONCENTRATIONS

One feature of the measured concentration differences for both gaseous and particulate species which stands out in all data is that the differences go through a minimum during the two-hour period beginning at 1600 hr. This sampling period includes the height of the evening rush hour. However, the explanation of this observation is that the wind speed typically is at a maximum during this sampling period. Therefore, the dilution of the emissions by advection is at a maximum at this time, and this dilution overshadows any emissions increases which result from the increased traffic density during the rush hour.

One exception to this general result is the CO concentration. Carbon monoxide emissions go up sharply as the vehicle speed is reduced. As a result, the increased CO emissions due to the reduced vehicle speed and the increased traffic density outweigh the dilution caused by the higher wind speeds.

7.0 DISCUSSION OF THE FILTER CHEMISTRY DATA

Two-hour filter samples were collected by both total particulate and respirable particulate samplers on both sides of the freeway. On the west side of the freeway, the total particulate samples were collected with an automatic sequential sampler (coded "Q") which used a 47 mm diameter membrane filter. At the ARB mobile laboratory on the east side, the 47 mm diameter total filters were coded "TF" and were changed manually. The sampling system which was part of the ARB laboratory was used rather than a second automatic sequential sampler because the manually operated unit was considered more reliable. On sampling day H (29 August 1974), a second automatic sequential sampler was operated on the roof of the ARB mobile laboratory to compare data from the TF and Q units, and to provide replication so that the sampling error could be estimated. Both the TF and Q samplers collect particulates smaller than about 20 μ m. The filters were analyzed for mass (TSP), sulfate, and by x-ray fluorescence for As, Br, Ca, Cr, Cu, Fe, Ga, Hg, K, Mn, Ni, Pb, Rb, S, Se, Sr, Ti, V, and Zn.

In addition, identical hi-vol samplers with cyclones were operated on each side of the freeway to collect filter samples of the particulates smaller than about 3.5 μm . The medium used in these samplers was Whatman 41 paper filters. They were analyzed by wet chemical methods for sulfate, nitrate, and ammonium. All analytical methods are described in the Final Report by AIHL (Appel and Wesolowski, 1976.).

7.1 FILTER FLOW CALIBRATIONS

It is believed that there are significant uncertainties in the calibration of the flow rates of the filter samplers. As a result, concentration differences which are small compared to the upwind concentrations can not be reliably determined from the data. However, the aerosol constituents, such as lead and bromine, which are emitted in significant amounts by the freeway traffic, show increases which are greater than the background values. In these cases, the emissions by the traffic can be determined.



One reason for believing that there are uncertainties in the calibration of the flow rates is that the data obtained on day H from the automatic sequential sampler on the roof of the ARB laboratory do not agree with the data collected at the same time by the TF unit at this location. This comparison is described on pages 41 through 43 of the AIHL Final Report (Appel and Wesolowski, 1975). The sulfate concentrations determined by wet chemistry are, on the average, 20% higher for the Q samples than the TF samples, and the sulfur concentrations determined by XRF are, on the average, 14% higher for the Q samples. These differences between the two samplers on the same side of the freeway are large compared to the sulfate or sulfur differences observed between the samples from opposite sides of the freeway.

The other reasons for questioning the flow rate calibrations come from the data themselves. The analysis of the data for the purpose of providing information about the flow rate calibrations is presented in the immediately following sections.

7.2 OVERVIEW OF THE FILTER CHEMISTRY DATA

Before examining the filter chemistry data for the separate chemical species, it is useful to look at the data as a whole to see what patterns can be found in them. In particular, it is useful to consider groups of elements having a common origin and to compare their observed concentration differences with the wind direction. If errors in flow rate calibration exist, these should influence the apparent concentration of all species on a given filter in the same way, and hence should produce discernable patterns in the data. For example, some species are emitted by the freeway traffic in significant amounts, hence the concentration differences for these compounds should be sensitive to the direction of the wind in relation to the highway. Other compounds are only negligibly influenced by the traffic, so concentration differences for them should be insensitive to the wind direction, but should depend critically on the flow rate calibrations. Once the properties of the data for these classes of compounds have been determined, the data for individual species can be interpreted with more confidence.



To aid in the interpretation of the data, the concentration difference across the freeway was calculated for each species for each filter pair, and these data are tabulated in Appendix B. These concentration differences were also normalized by dividing them by the NO_{X} concentration differences, as described in Section 6.3 The normalized concentration differences are also given in Appendix B. Any species which is emitted by the traffic at a rate which is proportional to the NO_{X} emission rate should have a normalized concentration difference which is constant, regardless of the traffic count and wind direction and velocity.

7.2.1 Total Filter Data

The total filters were analyzed for 20 species and elements plus the aerosol mass. Of these 20, the following eight elements were usually below the limit of detection: As, Cr, Ga, Hg, Rb, Se, Sr, and V. In addition, the following elements were below the limit of detection in the indicated fraction of the filter pairs: Cu, 20%; Mn, 10%; and Ti, 47%. The remaining nine species and the aerosol mass were measurable on essentially all of the filter pairs.

As the first step in checking the filter flow calibrations, the algebraic signs for the concentration differences were examined. The collection of seven filters a day for a total of 12 days resulted in 84 filters. For 17 of these of these collections times (all before noon), the average NO_{X} concentration was higher at the NWC laboratory, indicating that the wind blew predominantly from the east. Since the concentration differences were always calculated as the NWC concentration minus the ARB laboratory concentration, the concentration differences at these times for species which are importantly emitted by, or stirred up by, the traffic should be negative. At other times, the concentration of differences for these species should be positive. Lead is an example of an element whose concentration differences follow this pattern exactly, so that the normalized lead concentration differences are always positive.

For other species which are not emitted by the traffic in significant amounts compared to the ambient concentrations, it would be expected that the concentration differences would be positive if errors in the flow rate calibrations cause the concentration data from the ARB mobile laboratory to be too high, and the differences would be negative if the NWC readings were too high.



Table 7-1 A COMPARISON BETWEEN THE SIGN OF THE CONCENTRATION DIFFERENCES FOR EACH SPECIES AND THE AVERAGE WIND DIRECTION DETERMINED FROM THE SIGN OF THE NO $_{\rm X}$ CONCENTRATION DIFFERENCE

Number of Negative Concentration Differences Wind from the West Wind from the East (NO_X Difference Positive) (NO_X Difference Negative) Species Total Number of Differences 17 67 Continuous Monitor Data CNC 10(6)* 19(10) 03 00 56 3 17 3 14 CO S02 0(12)3(36)Total Particulate Sampler 2 8 Mass 17 0 Br 2 Ca 0 Cu 7 25 Fe 1 0 Κ 11 1 0(1)Mn 11 Νi 8 5 РЬ 17 0 S 3 36 S07 4 44 11 0 Respirable Particulate Sampler 7 3 NH_4 N03 1 13 2 S0₄ 2 Sample Patterns Auto Emissions 17 0 ARB Mobile Data High 0 0 NWC Mobile Data High 17 67 Random Signs 8.5 33.5

^{*}Numbers in parentheses give the number of missing data points.



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Table 7-1 gives the sign of the concentration differences for each species as a function of wind direction. As an aid in the interpretation of the data the results to be expected for species heavily influenced by automobile traffic, species uninfluenced by automobile traffic with one or the other sampling rate higher than calibration, or the result to be expected for a random distribution of differences are presented. It can be seen that the data for calcium and iron are nearly consistent with the hypothesis that these elments are not emitted by the traffic and that the filter flow rate at the ARB laboratory is higher than given by the calibration (or the flow rate at the NWC laboratory is lower). Potassium and manganese are almost as consistent with this hypothesis. All of these elements are important components of soil dust.

The algebraic signs of the lead and bromine concentration differences are completely consistent with the hypothesis that they are emitted by the traffic. Thus, lead or bromine could have been used as the tracer species instead of NO in this part of the analysis without changing the results. It appears that zinc arises both from the background and the traffic. When the wind was blowing from the west so that the NO differences were positive, both the sampling imbalance and traffic emissions would tend to cause positive zinc concentration differences, and the observed difference was positive in all 67 cases. However, when the wind was in the other direction, the sign of the zinc concentration difference was dominated by the auto traffic in 11 out of 17 cases, and by the sampling difference in the other six cases.

Except for sulfur and sulfate, to be discussed later, none of the 21 analytical results suggest that the filter sampling rate at the NWC mobile laboratory might be relatively too high. Instead, the results are consistent with the cumulative effects of a higher sampling rate at the ARB mobile laboratory and the emission or stirring up of a number of the species by the freeway traffic.

It should be possible to estimate the magnitude of the sampling error from the data for the elements which are apparently not influenced by the traffic and the wind direction. Because average differences for the afternoon are available in Appendix B, data for that time period were used in this estimation. Table 7-2 shows the observed difference divided by the concentration at the (downwind) ARB mobile laboratory for the elements Ca and Fe

Table 7-2
ESTIMATION OF SAMPLING IMBALANCE FROM THE CALCIUM AND IRON DATA

| Day | Afternoon | ARB-NAVY ARB |
|--|--|--|
| | Ca | Fe |
| A B C D E F G H I J | 0.66 0.37 0.59 0.71 0.69 0.41 0.45 0.56 0.58 | 0.66 0.46 0.61 0.74 0.66 0.40 0.40 0.41 0.61 |
| K L | 0.44 0.40 | 0.60 0.50 |
| Mean Std. Dev. | 0.52 0.12 | 0.56 0.13 |

Note: The data in the table give the concentration difference from Appendix B divided by the concentration observed at the ARB mobile laboratory.

for each day. It can be seen that the imbalance for the two elements is closely correlated. The overall average value for the concentration difference divided by ARB concentration is about 0.54. Therefore, the overall average for the Navy concetration divided by the ARB concentration is 0.46. In other words, the average Fe and Ca concentration observed at the Navy mobile laboratory was less than half that observed at the ARB mobile laboratory. This is an unreasonably large difference to be ascribed to flow calibration uncertainties.

The data in Table 7-3 provide a reasonably good clue as to some of the sources of these discrepancies. On Day H, 29 August 1974, a "Q" total particulate sampler like that at the NWC mobile laboratory was operated on the roof of the ARB mobile laboratory beside the intake of the "TF" sampler. Data from those two samplers for Ca, Fe, Pb, S, and $SO_4^=$ are compared in the table. The sulfur and sulfate data were compared on pp. 41 and 42 of the AIHL report, and it was con-

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Table 7-3

COMPARISON BETWEEN THE "TF" AND "Q" TOTAL PARTICULATE SAMPLERS AT THE ARB MOBILE LABORATORY

| Nominal Sampling Time | Calc µg/ | Calcium µg/m³ | Tr Pg | Iron µg/m³ | Le | Lead µg/m ³ | Su | Sulfur µg/m³ | Sulfate µg/m³ | ate m3 |
|--------------------------|-------------|------------------|----------|---------------|------|---------------------------|------|-----------------|------------------|-----------|
| 29 August 1974 | ഥ | 0 | ᄔ | o | TF | Ò | 보 | Ò | TF | Ò |
| 0080-0090 | 0.7 | 0.62 | 1.2 | 1.15 | 3.22 | 3.58 | 8.18 | 9.65 | 19.4 | 24.8 |
| 0800-1000 | 1.25 | 1.05 | 1.71 | 1.60 | 4.88 | 5.59 | 9.05 | 10.3 | 19.9 | 25.7 |
| 1000-1200 | 1.12 | 0.85 | 2.12 | 1.82 | 9.46 | 11.3 | 9.72 | 11.3 | 21.8 | 27.8 |
| 1200-1400 | 1.00 | 0.88 | 1.72 | 1.60 | 9.03 | 11.6 | 11.4 | 13.9 | 26.6 | 32.0 |
| 1400-1600 | 0.75 | 0.74 | 06.0 | 1.15 | 8.28 | 10.7 | 9.6 | 11.5 | 23.4 | 28.2 |
| 1600-1800 | 0.45 | 0.40 | 0.69 | 0.68 | 5.28 | 6.63 | 5.00 | 5.77 | 11.0 | 13.8 |
| 1800-2000 | 0.28 | 0.27 | 0.54 | 0.47 | 7.97 | 8.57 | 3.56 | 3.42 | 7.73 | 7.07 |
| Average | 0.79 | 0.69 | 1.27 | 1.21 | 6.87 | 8.28 | 8.12 | 9.40 | 18.6 | 22.8 |
| Average Q Average TF | 0.87 | 7 | 0.95 | 95 | į. | 21 | 1 | .16 | 1.0 | 1.23 |



cluded that a difference in flow calibration for the two samplers is the likely cause of disagreement. However, it will be noticed in Table 7-3 that the lead, sulfur, and sulfate values are higher in the data from the "Q" sampler, and the calcium and iron data are higher in the data from the "TF" sampler. The only exceptions are the iron data at 1400-1600 hr, and the sulfur and sulfate data at 1800-2000 hr.

In part, it is believed that these observations can be accounted for by differences in the large particle cut-off of the "TF" and "Q" samplers. The inlet tube of the "TF" sampler is 3 to 4 in diameter, and the inlet tube of the "Q" sampler is about 1 in diameter, so it is reasonable to expect that the "Q" sampler would see fewer very large particles. Calcium and iron are primarly due to soil dust, and are known to occur primarily in the large particle size mode. Therefore, the smaller concentrations measured by the "Q" sampler for these elements can reasonably be ascribed to the differing inlet efficiencies of the "TF" and "Q" samplers.

On the other hand, sulfur, sulfate, and most of the lead is known to be contained in particles small enough that the measured concentrations are not easily distorted by the geometry of the sample flow at the inlet. Therefore, it is also reasonable to presume that calibration errors in the flow rates for the two samplers combine to make the "Q" sampler appear to have about a 20% higher collection efficiency for small particles.

In summary, these data demonstrate that the total particulate samplers used on opposite sides of the freeway had different sampling efficiencies for large particles, and there are significant uncertainties in the sample flow rate calibrations. Therefore, the data for concentration differences determined from filter samples must be used with considerable caution.

7.2.2 Respirable Particulate Data

At the same time the total particulate filter samples were being collected, samples were being collected by a hi-vol with a cyclone to remove the particulates larger than about 3.5 μ m, so that only the respirable particulates were collected on the Whatman 41 filter paper. These filters were analyzed for sulfate,



nitrate, and ammonium. Based on the tabulations of the algebraic signs in Table 7-1, it seems that the data are best interpreted in terms of the hypothesis that none of these species are importantly affected by the freeway emissions, and that any imbalance in the filter flow favored the collection of larger samples than expected at the ARB mobile laboratory. None of the data correlate with the wind direction in such a way as to indicate that the freeway emissions had an important impact on the data.

No attempt has been made in this report to combine the respirable filter data with the total filter data to estimate the fraction of the sulfate in the size range below 3.5 μm . The reason is that the Whatman 41 filter papers used in the respirable samplers have an appreciably lower collection efficiency than the membrane filters used in the total particulate samplers, so that comparisons of this kind are not easily made.

7.3 SULFUR AND SULFATE

The data obtained from the total filters for elemental sulfur (by XRF) and sulfate (by the AIHL microchemical method) stand out in Table 7-1 as being different from the rest. If anything, the algebraic signs of the differences are most consistent with a sulfur and sulfate decrease across the freeway, similar to that observed for ozone. Since it has not been possible to set forth a reasonable mechanism by which such a process could actually occur on the freeway, it is suggested that the presence of an analytical interference should also be considered. For example, if lead or bromine were to interfere with these determinations in a negative sense, this would provide an explanation of the observation. However, the signs of the sulfur and sulfate data given in Table 7-1 are sufficiently close to a random distribution that it would be difficult to use these data to prove that an analytical interference exists. The way the sulfur and sulfate data shift with the wind shift is only suggestive. None of the data from the other species determined on the total particulate filters support the possibility that the sulfur and sulfate differences are due to errors in the flow rate calibrations. However, none of the species measured are known to be both in the fine particle size range and unaffected by a major freeway.



7.4 LEAD AND BROMINE

Lead is the component of the aerosol whose concentration difference resulting from the traffic was most reliably measured. After 1200 hrs, when the wind was consistently from the west, the average lead concentration difference was 6.6 $\mu g/m^3$. In general, the upwind lead concentrations were at or near $1\mu g/m^3$, so the differences were generally large compared to the background levels.

The lead emissions are due to the use of tetraethyl lead in gasoline to increase its octane rating. In general, regular gasoline contains 1.5 gm/gal and the premium grades contain 2.5 gm/gal. To minimize engine fouling by this lead, organic halogen-containing compounds are added to the gasoline. In this study, Br was included in the analyses, and an average increase of 2.6 $\mu \text{g/m}^3$ in bromine concentration was found in the data taken after 1200 hrs. Daily averages for the data taken after 1200 hrs are given in Table 7-4 for the normalized lead concentration differences, and for the ratio of the bromine and lead differences. The latter ratio is given on a mole basis, and it can be seen that very nearly one mole of bromine is contributed to the aerosol for each mole of lead. Lead chlorobromide is a compound present in automobile exhaust, and it contains a 1:1 mole ratio for lead and bromine just as observed in the concentration differences in this study. In contrast, it was found in the aerosol at the upwind side of the freeway that the average ratio of bromine to lead on a mole basis was 0.6.

The daily average normalized lead concentrations in Table 7-4 are quite consistent throughout the study, and have an average value of 6.58 $\mu g/m^3$ Pb per ppm NO_X. The standard deviation of daily averages of this ratio about this mean is less than 8% of the mean.

7.5 REDUCED SULFUR SPECIES

X-ray photoelectron spectroscopy (XPS or ESCA) was used to obtain a second value for the amount of sulfur contained in the total particulate samples. The XRF values were typically higher than the wet chemical sulfate analyses for both the up and downwind samples. The average ratio of wet chemical sulfur

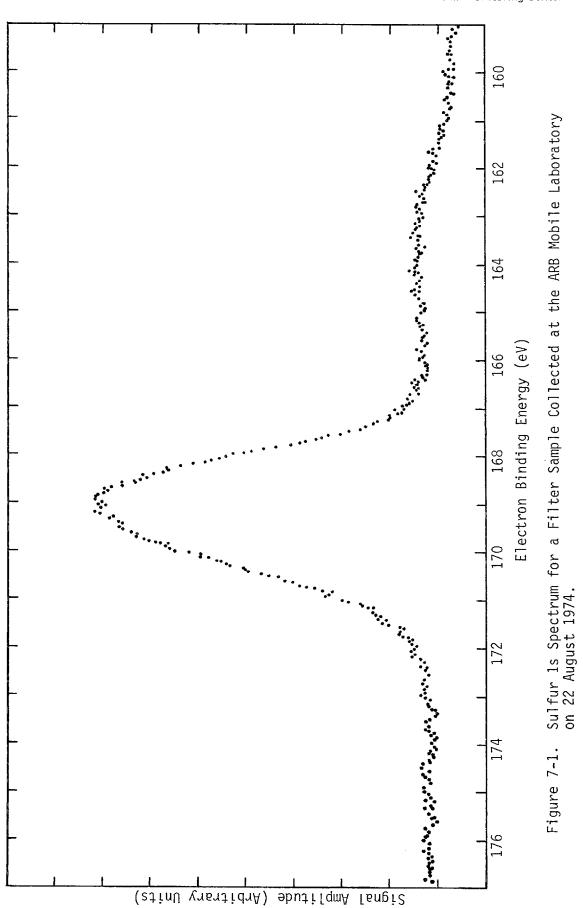
Table 7-4 RATIOS OF THE AVERAGE CONCENTRATION DIFFERENCES FOR THE 1200 TO 1800 HOUR PERIOD FOR BROMINE AND LEAD AND FOR LEAD AND NO $_{\rm X}$

| Day. | $\frac{\Delta Br}{\Delta Pb}$ ($\frac{mole}{mole}$) | $\frac{\Delta Pb}{\Delta NO_X}$ $(\frac{\mu g/m^3}{ppm})$ |
|-----------|---|---|
| А | 0.96 | 6.5 |
| В | 1.16 | 5.6 |
| С | 1.04 | 6.2 |
| D | 0.85 | 7.3 |
| E | 0.91 | 7.1 |
| F | 1.16 | 6.5 |
| G | 1.09 | 6.9 |
| Н | 0.97 | 6.4 |
| I | 1.07 | 7.0 |
| J | 1.04 | 7.1 |
| K | 1.04 | 6.2 |
| L | 0.98 | 6.1 |
| Mean | 1.02 | 6.58 |
| Std. Dev. | 0.09 | 0.51 |

to XRF sulfur for the NWC mobile laboratory was found to be 85.5%. For the ARB mobile laboratory wet chemical sulfur to XRF sulfur ratio was found to be 79.2%. The difference of +6.3% between the upwind and downwind ratios suggests the possibility that a small amount of non-sulfate particulate sulfur could be associated with vehicular traffic. The AIHL data analysis indicates that the contribution of non-sulfate sulfur species typically increased by 0.3 μ g/m³ across the freeway (Appel and Wesolowski, 1975).

The possibility that the traffic was contributing a small amount of reduced sulfur to the total particulate samplers was investigated by XPS. A portion of each up and downwind total particulate sample collected during episode D was subjected to XPS analysis. Episode D was selected since this day had a sea breeze blowing across the freeway for the entire sampling episode.

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A comparison of the wet chemical sulfate and x-ray fluorescence analyses for the two-hour samples collected after 1200 hrs during episode D showed the XRF analysis sulfur to be an average of 10% larger per sample at the NWC mobile laboratory, and 15% larger per sample at the ARB mobile laboratory. This corresponds to an average increase of about 0.5 μ g/m³ of particulate sulfur which could be attributed to freeway traffic.

The XPS spectra of the sulfur on the surface of the particulate samples showed that indeed the downwind particles did contain a small amount of reduced sulfur. As shown in the example in Figure 7-1, there was a major sulfur peak at 169 eV characteristic of $SO_4^=$ and a small broad reduced sulfur peak at 164-165 eV corresponding to a mixture of surface sulfides and elemental sulfur. The upwind samples from the NWS mobile laboratory did not show any measurable reduced sulfur as shown in Figure 7-2. A semi-quantitative number for the amount of sulfur present on the surface of the particles can be obtained by taking the ratio of the reduced sulfur peak intensity to that of the $\mathrm{SO}_4^=$ electron peak. The values for the ratio of $S0_4^{=}$ to total sulfur found by this technique are recorded in Table 7-5 along with the observed ratios of the wet chemical sulfur values to those from the XRF total sulfur analyses. The sulfur values determined by the XPS technique are quantitative only insofar as the surface of the particles represent the bulk properties of the sample. Since the samples analyzed in this study were a combination of background material and freeway generated particles, the surfaces were not necessarily representative of the bulk, hence the XPS sulfur values can only be treated as semi-quantitative in this instance.

As can be seen in Table 7-5, the XPS data show about 8% of the downwind sulfur to be in the reduced form. Unfortunately, the size of the experimental errors involved in these sampling techniques are large enough that no valid quantitative value can be placed upon the amount of reduced sulfur actually added to the total sulfur content of the particles by the freeway traffic. However the XPS data do confirm that reduced sulfur is contributed by the traffic, with the combination of all data from the three analysis techniques indicating that this con-

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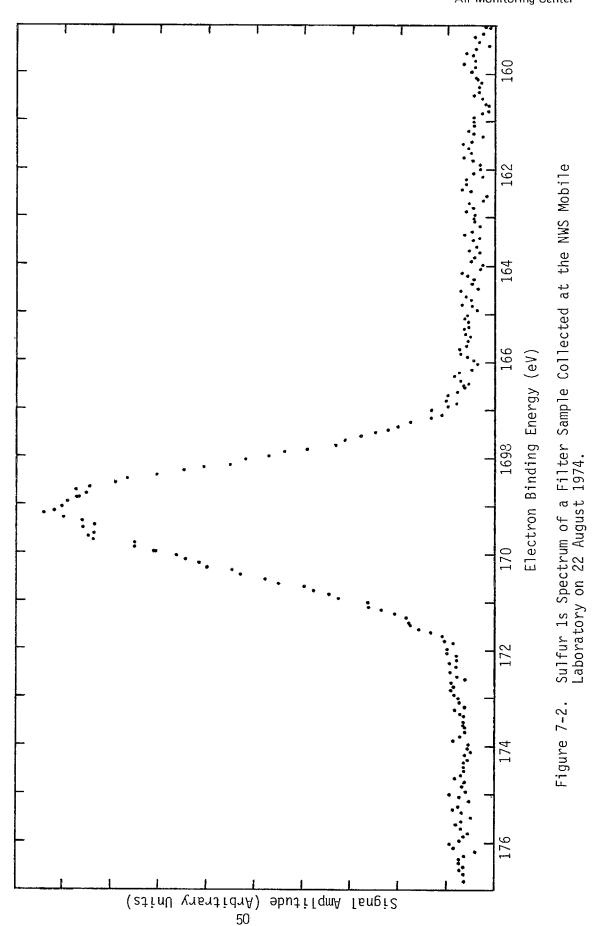
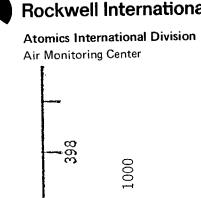
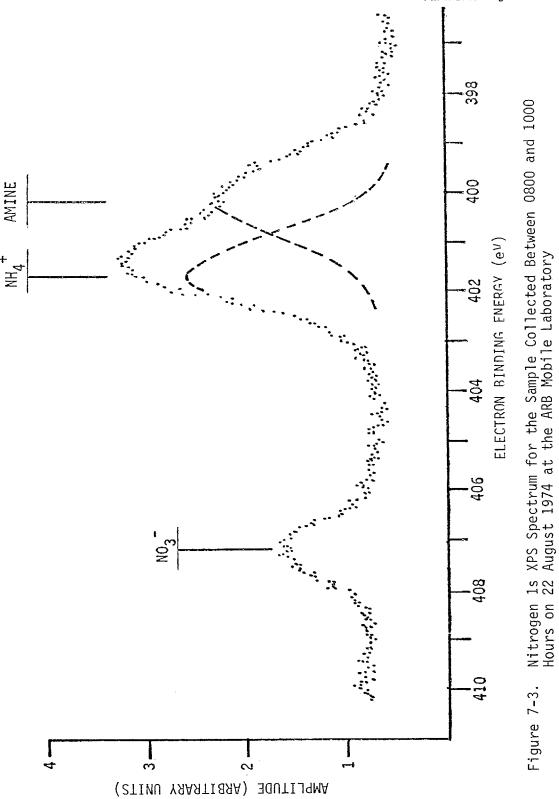


Table 7-5

COMPARISON OF WET CHEMICAL, X-RAY FLUORESCENCE,
AND X-RAY PHOTOELECTRON ANALYSES OF TOTAL FILTER SAMPLES FOR DAY D

| | Wet Chemica XRF | $\frac{1}{S} \frac{S_4}{as} = \frac{S}{S}$ | XPS c | 0 <mark>4</mark> tal |
|--------------------------|---------------------------|--|---------------------------|---------------------------|
| Nominal Sampling Time | NWC Mobile (west side) | ARB Mobile (east side) | NWC Mobile (west side) | ARB Mobile (east side) |
| 600 | 0.92 | 0.91 | 1.0 | 0.93 |
| 800 | 0.98 | 0.92 | 1.0 | 0.93 |
| 1000 | 0.90 | 0.92 | 1.0 | 0.91 |
| 1200 | 0.94 | 0.84 | 1.0 | 0.90 |
| 1400 | 0.79 | 0.88 | 1.0 | 0.94 |
| 1600 | 0.98 | 0.81 | 1.0 | 0.91 |
| 1800 | 0.90 | 0.87 | 1.0 | 0.92 |
| Overall Average | 0.92 | 0.88 | 1.0 | 0.92 |
| Average After 1200 Hr | 0.90 | 0.85 | 1.0 | 0.92 |







tribution is $\leq 0.3 \,\mu\text{g/m}^3$ of sulfur on the average.

The probable formation mechanism for the reduced sulfur species is the surface reduction of SO_2 to a surface sulfide on soot particles in the vehicle exhaust. This mechanism has been demonstrated by Novakov, Chang, and Harker (1974) through the adsorption of SO_2 on graphite particles.

7.6 REDUCED NITROGEN SPECIES

The XPS analysis of the total particulate samples collected during episode D also included a determination of the chemical states of nitrogen present on the surface of the samples. A XPS spectrum for the nitrogen 1s electron region is shown in Figure 7-3 for the downwind ARB trailer sample between 0800 and 1000 hours. This spectrum shows nitrogen to be present in three forms. The three nitrogen peaks were identified using the assignments of Chang and Novakov (1975) which indicate that the peak at 407 eV belongs to NO_3^- , the peak at 402 eV to NH_4^+ , and the peak at 400 eV to a reduced nitrogen species similar to an amine or an amide $(N_{\rm x})$.

An assessment of the freeway contribution to the N_X species at 400 eV can be made on the basis of these data; however, the XPS analyses are not valid in this case for the nitrate or ammonium forms of nitrogen. The nitrate data are not valid because of a nitrate impurity in the Gelman GA-1 filter membranes, which interferes with the analysis. In the case of ammonium, it has been shown by Chang and Novakov that surface ammonium in ambient particulates is volatile at room temperature in the vacuum of the XPS spectrometer. Hence, the XPS spectrum only shows that fraction of the surface ammonium which is present in a non-volatile form and, consequently, gives a consistently low value for ammonium content when compared with set chemical analyses.

The overlapping NH_4^+ and N_X 1s electron peaks were deconvoluted to obtain the relative contribution of each to the total peak area based upon the known peak shapes and locations. Approximate N_X concentrations were then calculated by taking the ratio of the N_X peak amplitude to that of the Pb 4d electron and normalizing for relative sensitivities and the concentrations of Pb observed by the XRF analyses. These data are listed in Table 7-6.



Table 7-6

AMINE- OR AMIDE-LIKE REDUCED NITROGEN OBSERVED BY XPS ANALYSES ON THE TOTAL PARTICLE SAMPLES COLLECTED DURING DAY D

| Nominal Sampling Time | N _x μg/m ³ Relative NWC Mobile (west side) | to XRF Pb Analyses ARB Mobile (east side) | N _X Concentration Difference |
|--------------------------|--|---|---|
| 0600-0800 | 0.6 | 1.1 | 0.5 |
| 0800-1000 | 1.2 | 1.3 | 0.1 |
| 1000-1200 | 0.2 | 1.1 | 0.9 |
| 1200-1400 | 0.7 | 1.0 | 0.3 |
| 1400-1600 | 0.4 | 0.9 | 0.5 |
| 1600-1800 | 0.2 | 0.6 | 0.4 |
| 1800-2000 | 0.4 | 0.6 | 0.2 |
| Average | 0.53 | 0.94 | 0.41 |



The results show a consistent increase in the concentration of the $\rm N_{\chi}$ species across the freeway for the entire episode, which is in agreement with the behavior of the tracer species $\rm NO_{\chi}$ and Pb. Though the magnitude of the average concentration change is small (< 0.5 $\mu \rm g/m^3$) the relative enhancement of the $\rm N_{\chi}$ species is quite large, with the average change across the freeway being about 80% of the upwind value. This indicates that the amine or amidelike reduced nitrogen species is indeed traffic related as suggested by Chang and Novakov (1975) who proposed that this species is formed as a primary pollutant from combustion through the surface reactions of NO and NH3 with hot soot particles.

7.7 MANGANESE

At the time these data were taken, manganese was not a common additive to motor fuel, but the atmospheric manganese concentrations were almost always above the limit of detection. Therefore, in this case, the data bank does serve its intended purpose of providing baseline concentration data before the advent of emission changes due to new emission control measures.

The overall average concentration difference for manganese during the afternoon is $0.008~\mu g/m^3$, or about 1/100 the difference for iron. This ratio is comparable to that for the composition of the earth's crust, so it is reasonable to presume that the Fe and Mn come from similar sources. Therefore, a very low upper limit can be put on the manganese emissions by freeway traffic in September of 1974.

7.8 CHEMICAL COMPOSITION OF THE MASS DIFFERENCE

This section combines the data in the previous sections to obtain an estimate of the fraction of the observed particulate mass difference which can be accounted for by the species whose concentrations were determined. This analysis is based on data collected only after noon, because in the afternoon the wind blew uniformly from the west, so the particulate mass is most easily determined during this time.



The overall average mass increase during the afternoon of the 12 sampling days was 29 $\mu g/m^3$. On the average, 6.6 $\mu g/m^3$ of this was Pb, and 2.6 $\mu g/m^3$ was Br. The next most important contributors were Fe and Ca, with 0.6 and 0.3 $\mu g/m^3$ average differences, respectively. The average difference for zinc was 0.04 $\mu g/m^3$, and all other species which were determined contributed less than 0.1 $\mu g/m^3$. Thus, about one-third of the observed total is accounted for.

Additional mass can be accounted for by other species known to be present, for example, the Cl in PbClBr, and the silicates and carbonates associated with such metals as Fe and Ca.

It is believed that a large portion of the remaining mass not accounted for above is carbonaceous, and is made up of such materials as soot from diesels, oil smoke, particles from tire wear, etc. This belief is confirmed by x-ray photoelectron spectroscopic analysis, which showed carbon to be the major species present in the particulate samples.



8.0 AEROSOL PARTICLE SIZE DISTRIBUTION

Measurements of the aerosol particle size distribution were made by optical particle size counters (OPC) and electrical aerosol analyzers (EAA). At the time this work was done, the methods of operating the instrument and reducing the data from the Model 3030 EAA were still under development. On examining the then recommended data reduction procedure, it quickly became apparent improvements in it could easily be made. Therefore, the work described in Appendix C was done.

The major problem with the existing EAA data reduction scheme was that it was based on the assumption that a monodisperse aerosol would produce a signal (current difference) in only one instrument channel. From the calibration data, this is clearly not the case (Liu and Pui, 1975). One result of this assumption is that the best constants for the Lui-Pui data reduction scheme depend on the aerosol size distribution, and can vary by as much as a factor of two or three. Another result is shown in Figure 3 of Appendix C, where the qualitative relation between the aerosol concentration in the size range corresponding to instrument channel 5 and the aerosol concentration in the neighboring size ranges is distorted. It is believed that these problems are resolved by the new data reduction scheme.

Figures 8-1 through 8-7 and also Figure 4 in Appendix C give the result of fits to selected one-hour average data obtained by the Model 3030 EAA in the NWC mobile laboratory. The resulting "best fit" parameters are given in Table 8-1. The figures contain some conventions which it may be helpful to the reader to explain in detail.

The goal of the fitting procedure described in Appendix C is to find an assumed bimodal log-normal distribution which leads to a calculated instrument response that is a "best fit" to the observed instrument response. In other words, the current differences calculated from assumed aerosol size distribution should agree with the experimental current differences. In this work, the best fit was determined primarily by a visual comparison of plots of the experimental and observed current differences. Before making this comparison,

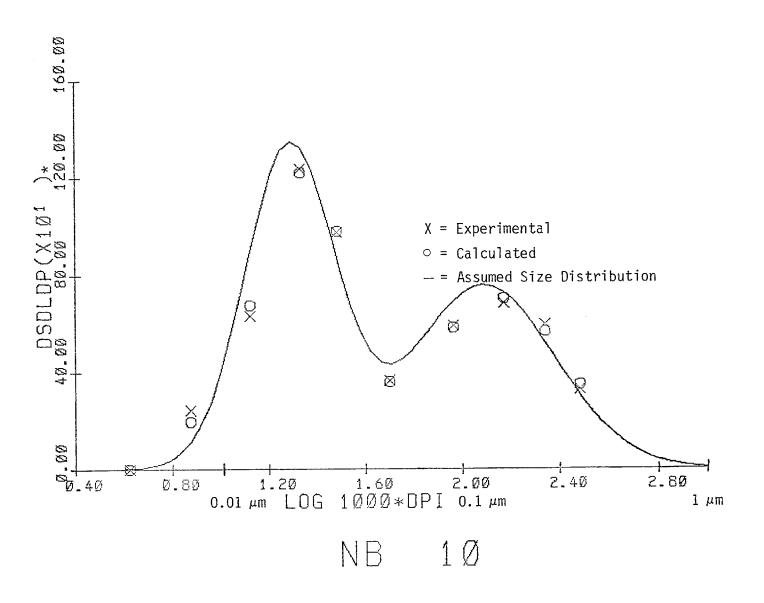


Figure 8-1. Fit to One-Hour Average EAA Data Beginning at 1000 hr on 20 August 1974
* $\frac{\Delta S}{\Delta \log D}$ in μm^2 cm⁻³. The numbers on the ordinate should be multiplied by

 $\Delta \log D_{\rm p}$ in μ m $^{\circ}$. The numbers on the ordinate should be the power of ten in parentheses.

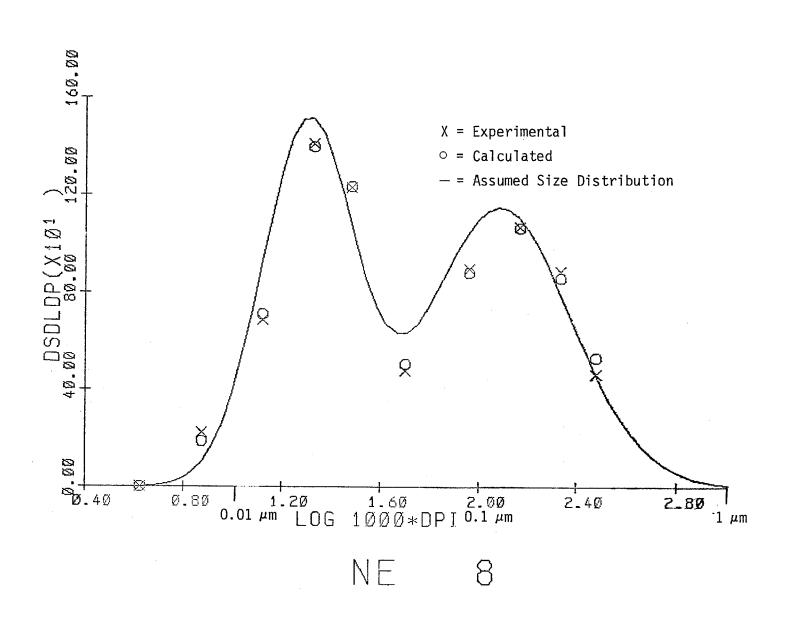


Figure 8-2. Fit to One-Hour Average EAA Data Beginning at 800 hr on 23 August 1974

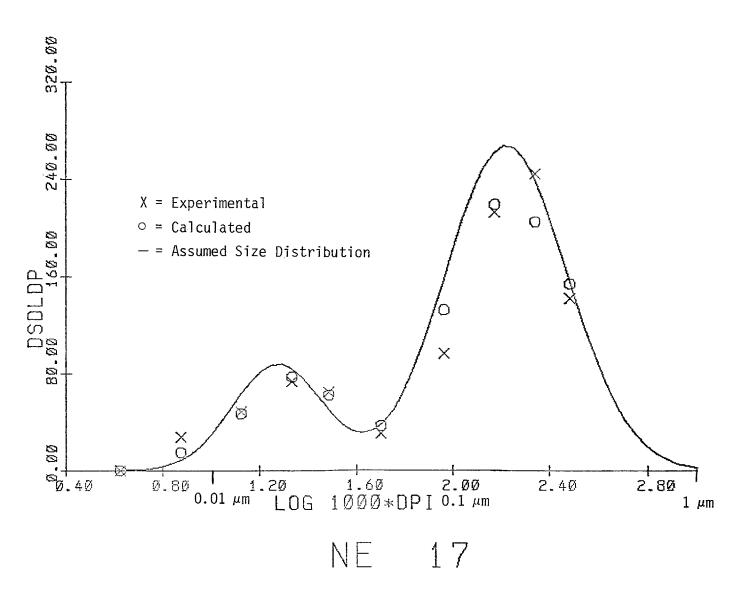


Figure 8-3. Fit to One-Hour Average EAA Data Beginning at 1700 Hr on 23 August 1974

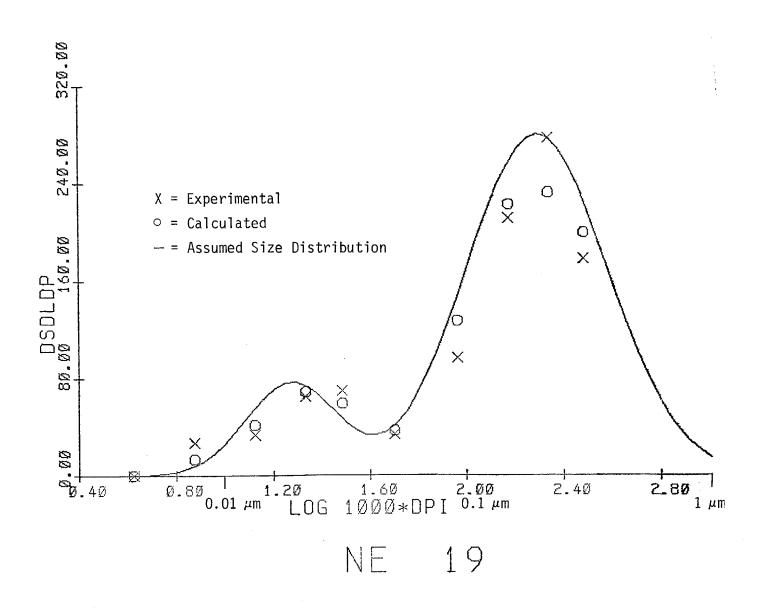


Figure 8-4. Fit to One-Hour Average EAA Data Beginning at 1900 Hr on 23 August 1974

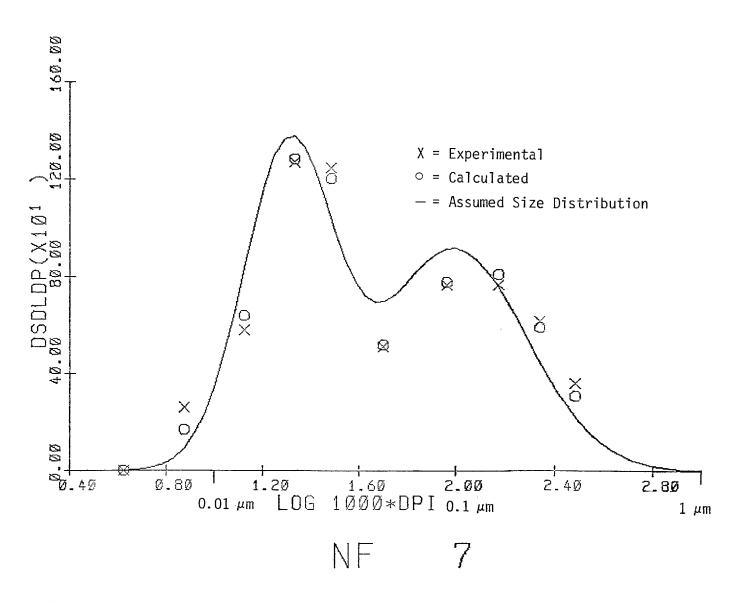


Figure 8-5. Fit to One-Hour Average EAA Data Beginning at 0700 Hr on 27 August 1974.

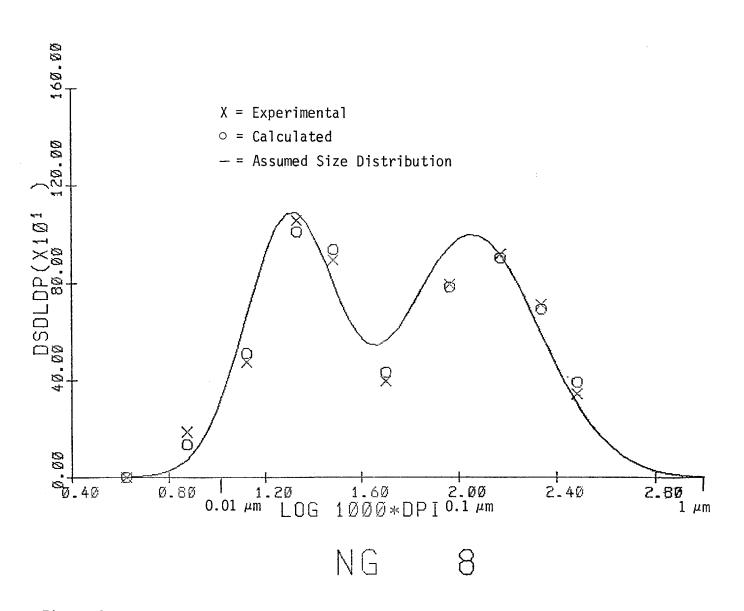


Figure 8-6. Fit to One-Hour Average EAA Data Beginning at 0800 Hr on 28 August 1974.

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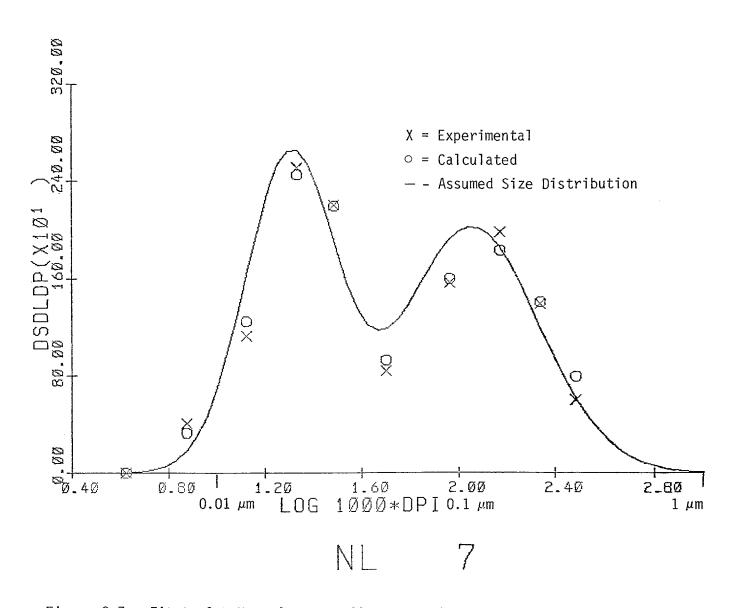


Figure 8-7. Fit to One-Hour Average EAA Data Beginning at 0700 Hr on 5 September 1974.

Table 8-1

DATA FROM PARTICLE SIZE FITS IN FIGURES 8-1 THROUGH 8-7

| Nuclei Mode | | Accumulation Mode | | | Hour Average | | |
|----------------|---------|-------------------|---------------------------|---------|-----------------|---------------------------|-------------------|
| Sample Code | Dg | σ | Particle Concentration | Dg | σ | Particle Concentration | NOx Difference |
| Day-Hr | μ m | | 10 ⁴ per cc | μ m | | 10 ⁴ per cc | ppm |
| NB10 | 0.0135 | 0.43 | 75. | 0.05 | 0.67 | 2.9 | -0.186 |
| NE8 | 0.014 | 0.43 | 78. | 0.05 | 0.67 | 4.4 | -0.275 |
| NE17 | 0.013 | 0.43 | 5.3 | 0.085 | 0.58 | 0.38 | +0.190 |
| NE19 | 0.013 | 0.43 | 4.6 | 0.08 | 0.67 | 0.42 | +0.371 |
| NF7 | 0.014 | 0.43 | 69. | 0.04 | 0.67 | 5.4 | -0.268 |
| NG8 | 0.014 | 0.43 | 56. | 0.05 | 0.64 | 3.9 | -0.148 |
| NL7 | 0.014 | 0.43 | 137. | 0.05 | 0.64 | 7.9 | -0.598 |
| NL9 | 0.0125 | 0.43 | 67. | 0.05 | 0.55 | 6.9 | -0.156 |

Note: The values of Dg are for log-normal distributions on a particle number basis. The plot for NL9 is figure 4 of Appendix C.

the current differences were multiplied by the weighting factors in the Liu-Pui data reduction procedure which convert the current difference in each instrument channel into the aerosol surface area in the corresponding size range $(\Delta S/\Delta \log\,D_p).$ It is these weighted data points which appear in the figures. The quality of each fit can be observed from how well the calculated and experimental points fall on each other. If the Liu-Pui data reduction procedure were exactly correct, the points would define the aerosol surface as a function of particle size curve for the observed one-hour average aerosol.

As described in Appendix C, the assumed aerosol size distribution used to calculate the fits is composed of a series of monodisperse aerosols. This assumed size distribution is represented in the figures by a series of points which are connected by straight line segments. The points are closely enough



spaced that line segments almost appear to be a smooth curve. This curve represents the aerosol size distribution which gives the instrument response shown by the circles in each figure. The separation between the curve and the circles is a measure of the bias introduced by the conventional Liu-Pui data reduction method.

An examination of the data in the figures and in Table 8-1 leads to the following conclusions:

- The EAA data can be fit very well by a bimodal log-normal size distribution.
- The best fit log-normal parameters from the Liu-Pui data reduction procedure can be somewhat distorted.
- The geometric mean diameter and the sigma of the nuclei mode and the accumulation mode aerosol are very constant from day-to-day. (This observation has been pointed out many times by K. T. Whitby of the University of Minnesota.) A possible exception to this is that the accumulation mode aerosol has a somewhat larger geometric mean size in the two afternoon data points included in this analysis.
- The number of aerosol particles in the nuclei mode on the downwind side of the freeway divided by the hour-average increase in NO_X across the freeway is about 3 x 10^6 particles cm⁻³ ppm⁻¹. This quantity is the normalized concentration difference for nuclei mode aerosol due to traffic, and is analogous for the normalized concentration differences for other species tabulated in Appendix B.

At the time this reduction of the aerosol data was undertaken, it was expected that the filter chemistry data would be more useful than they turned out to be, and that a further comparison of physical aerosol size measurements with aerosol chemistry data would be carried out. When the true nature of the filter chemistry data became known, this part of the work was reduced in scope.

A similar analysis has not been performed for the data from the Model 3000 EAA in the ARB mobile laboratory. The primary reason for this is that this instrument has not been calibrated with monodisperse aerosols in the same way that Liu and Pui have calibrated the Model 3030 EAA.

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APPENDIX A

DESCRIPTION OF THE MAGNETIC TAPE

DATA BASE AND A SAMPLE OF THE DATA



This Appendix contains a description of the contents and format of the magnetic tape data base which accompanies the Final Report. This information allows the reader to determine if the data base contains information of interest to him, and if so, how to access that information on the magnetic tapes.

The data base consists of three reels of magnetic tape. Two reels contain the 10-minute data, and the third reel contains the one-hour and two-hour average data. The two-hour averages were calculated to allow a direct comparison between the continuous instrument data and the results from the chemical analysis of the two-hour filter samples.

All data tapes are 9-track, ASCII, unblocked, with even parity and 800 BPI. Each of the 48 files are separated by one end of file mark. The data files are identified by the day and site code described in Table 5-3. The files included on tape are:

10-minute data files: OA-OL, NA-NL (24 files)

1-hour average files: A-L (12 files) 2-hour average files: A-L (12 files)

10-Minute Value Files - 80 Character ASCII Record

One file has been generated for the data from each day for each of the ARB and NWC mobile laboratories. The sampling locations are described in Section 5.1 and sampling days and their codes are listed in Table 5-3. Each file contains 10-minute values of analog data obtained through a multiplexor (MUX data), sulfur dioxide data, and particle data. In addition, the ARB mobile files also contain traffic count data.

Each record within a file contains self-identification by site, episode, date and time. Time is defined by hour and by minute, in multiples of 10 minutes. Each record represents the 10-minute value for a particular parameter, and is defined by data type code (MUX, particle, or traffic), channel number, and data values. The parameters available, with corresponding channel numbers,



are listed in Table A-1. The three types of data are merged by time, so that all data for time 0600, in order MUX, particle, traffic, exist in the file before the data for time 0610. The calibration constants and units for the NWC files are dummies; the actual values were not available.

The three types of data records are identical for characters 1-15, as shown in Table A-2. For type 3 (MUX) data, type 4 (particle) data and type 5 (traffic) data, the formats for characters 16-80 are shown in Table A-3.

Following is an example of each site's 10-minute value files:

| 0A74 8143 | 600 i | 0.155E 02 | 0.100E 03 | 0.117E 03 | |
|------------|---------|------------|------------|-----------|-----------|
| 0A74 8143 | | 0.000E 00 | 0.644E 01 | 0.155E 01 | |
| OA74 8143 | | 0.000E 00 | 0.900E 01 | 0.314E 01 | |
| 0A74 8143 | 600 4 · | -0.178E 02 | 0.556E 03 | 0.183E 02 | |
| OA74 8143 | 600 5 · | -0.178E 02 | 0.556E 03 | 0.242E 02 | |
| OA74 8143 | 600 7 | 0.000E 00 | 0.200E-03 | 0.324E-03 | |
| '0A74 8143 | 600 0 | 0.000E 00 | 0.144E 02 | 0.514E-03 | |
| 0A74 8143 | 600 9 | 0.000E 00 | 0.147E 03 | 0.000E 00 | |
| OA74 8143 | 60012 | 0.000E 00 | 0.100E 01 | 0.298E-01 | |
| 0A74 8143 | 60013 | 0.000E 00 | 0.100E 00 | 0.875E-02 | |
| 0A74 8143 | 60014 | 0.000E 00 | 0.100E 00 | 0.318E-01 | |
| 0A74 8143 | 60015 | 0.000E 00 | 0.100E 00 | 0.441E-01 | |
| 0A74 8143 | 60016 · | -0.225E 02 | -0.105E 04 | 0.769E 02 | |
| 0A74 8144 | 600 1 | 0.100E-01 | 0.178E-01 | 0.284E 06 | 0.580E 06 |
| 0A74 8144 | 600 2 | 0.178E-01 | 0.316E-01 | 0.505E 05 | 0.185E 06 |
| 0A74 8144 | 600 3 | 0.316E-01 | 0.562E-01 | 0.780E 04 | 0.645E 05 |
| 0A74 8144 | 600 4 | 0.562E-01 | 0.100E 00 | 0.311E 04 | 0.245E 05 |
| 0A74 8144 | 600 5 | 0.100E 00 | 0.178E 00 | 0.142E 04 | 0.113E 05 |
| OA74 8144 | 600 G | 0.178E 00 | 0.316E 00 | 0.576E 03 | 0.600E 04 |
| OA74 8144 | | 0.316E 00 | 0.422E 00 | 0.139E 03 | 0.385E 04 |
| 0A74 8144 | 600 B | 0.422E 00 | 0.562E 00 | 0.106E 03 | 0.100E 01 |
| 0A74 8144 | 600 9 | 0.562E 00 | 0.100E 01 | 0.6025 02 | 0.100E 01 |
| 0A74 8144 | 60010 | 0.100E 01 | 0.178E 01 | 0.299E 01 | 0.100E 01 |
| 0A74 8144 | | 0.1785 01 | 0.316E 01 | 0.1595 00 | 0.100E 01 |
| 0A74 8144 | 60012 | 0.3165 01 | 0.562E 01 | 0.8255-01 | 0.100E 01 |

The ARB site example (OA) contains both MUX (type 3) and particle (type 4) data for the time 0600 - 0609, 8/14/74. Channel 1, type 3, represents wind direction, and its value for the time period is 117° . The A and B constants are 15.5 and 108, respectively. Channel 1, type 4, data represents particle data of mean diameter size .0133 μ ; the count is $284000/\text{cm}^3$. The lower size boundary for this class is .01 μ ; the higher boundary is .0178 μ . The Dn/Di value (a scaling factor) is 580000.



Table A-1

10-MINUTE DATA BASE CHANNEL/MNEMONIC CORRESPONDENCE

| Mnemonic | ARB Channel No. | NWC Channel No. |
|---|---------------------------------|-----------------|
| Type 3 Data (MUX) | | |
| WDIR (wind direction)(degrees) | 1 | 3 |
| WSPD (wind speed)(km/hr) | 2 | 4 |
| WSIG (wind sigma)(degrees) | 3 4 | 1 |
| TOUT (outside temperature)(°C) | 5 | 1 |
| TIN (inside temperature)(oC) BSCAT (light scattering coefficient)(/ | | 6 |
| UVRAD (ultra violet radiation)(cal/cm ² |) ' . | |
| BBRAD (broad band solar radiation) | 9 | |
| (cal/cm ² /min) | _ | 0 |
| CNC (condensation nuclei counter)(no | o/cm ³) 11 12 | 8 7 |
| 03 (ozone)(ppm) | 13 | 9 |
| NO (nitric oxide)(ppm) NO2 (nitrogen dioxide)(ppm) | 14 | 3 |
| NOX (total oxides of nitrogen)(ppm) | 15 | 10 |
| RELHUM (relative humidity)(%) | 16 | 2 |
| CO2 (carbon dioxide)(ppm) | 17 | 11 |
| SO2 (sulfur dioxide)(ppm) | 20 | 20 |
| HCTOT (total hydrocarbons)(ppm) | 21 22 | |
| CH4 (methane)(ppm) CO (carbon monoxide)(ppm) | 23 | 5 |
| C2H4 (ethylene)(ppm) | 24 | |
| Type 4 (particle data, by mean diameter | in μ m) | |
| D = .0133 | 1 | |
| D = .0237 | 2 | |
| D = .0421 | 1 2 3 4 5 6 7 | |
| D = .0750 D = .133 | 4 5 | |
| D = .133 D = .237 | 6 | |
| D = .365 | | |
| D = .487 | 8 | 8 |
| D = .750 | 9 | 9 |
| D = 1.33 | 10 11 | 10 11 |
| D = 2.37 D = 4.21 | 12 | 12 |
| D = .0042 | ± - | 21 |
| D = .0075 | | 22 |
| D = .0133 | | 23 |
| D = .0215 | | 24 25 |
| D = .0306 D = .0502 | | 26 |
| D = .0502 D = .0917 | | 27 |
| D | | |



Table A-1 (Continued)

| M | nemonic | ARB Channel No. | NWC Channel No. |
|-------|---|-----------------|-----------------|
| | D = .149 D = .219 D = .306 | | 28 29 30 |
| Note: | Diameters .487 μ - 4.21 μ representable other channels are Electrical | | |

Table A-2
FORMAT FOR CHARACTERS 1-15, 10-MINUTE FILES

| Character | Identification | Possible Values | Format |
|----------------|-------------------|---|--------|
| 1-2 | Site, Episode | Site = N,O (Navy,Rockwell) Episode = A-L | A2 |
| 3-4 | Year | 74 | 12 |
| 5-6 | Month | 8,9 | 12 |
| 7-8 | Date | 14,20-23,27-30,3-5 | I2 |
| 9 | Туре | 3,4,5 (MUX,particle,traffic) | I1 |
| 10-11 | Hour | 06-20 | 12 |
| 12-13 14-15 | Minute Channel | 0,10,20,30,40,50 1-40 | 12 |
| 16-80 | See Table A-3 | | 60A1 |

Table A-3
FORMAT FOR CHARACTERS 16-80, FOR 10-MINUTE FILES
BY DATA TYPE

| | Character | Identification |
|--------------|--|---|
| Type 3 (MUX) | 4 (5X, E10.3) 16-20 21-30 31-35 36-45 46-50 51-60 61-80 | Blank Offset Blank Slope Blank Value in Engineering Units Blank |
| | | Brank |



Table A-3 (Continued)

| Character | Identification |
|---|--|
| Type 4 (particle): 4 (5X,E10.3) 16-20 21-30 | Blank Lower Boundary (Limit) |
| 31-35 36-45 46-50 51-60 | Blank Upper Boundary (Limit) Blank Number of particles, in concen- tration/cm ³ |
| 61-65 66-75 76-80 | Blank Calibration Factor (DN/DI scaling factor) Blank |
| Type 5 (traffic): 30X, A1, 4X, E10.3, 5X | |
| 16-45 46 47-50 51-60 61-80 | Blank Direction of Flow N,S Blank Number of Cars, Observed Blank |

| NA74 8143 6 | 0 1 | 0.000E 00 | 0.100E 01 | 0.202E 02 |
|--------------|----------------|-----------|-----------|-----------|
| NA74 8143 6 | 02 | 0.000E 00 | 0.100E 01 | 0.719E-01 |
| NA74 8143 6 | 03 | 0.000E 00 | 0.100E 01 | 0.291E 03 |
| NA74 8143 6 | 94 | 0.000E 00 | 0.100E 01 | 0.122E 01 |
| NA74 8143 6 | 05 | 0.000E 00 | 0.100E 01 | 0.106E 01 |
| NA74 8143 6 | 06 | 0.000E 00 | 0.100E 01 | 0.423E 01 |
| NA74 ,8143 6 | 07 | 0.000E 00 | 0.100E 01 | 0.223E-02 |
| NA74 8143 6 | 0 8 | 0.000E 00 | 0.100E 01 | 0.425E 07 |
| NA74 8143 6 | 0 9 | 0.000E 00 | 0.100E 01 | 0.851E-01 |
| NA74 8143 6 | 010 | 0.000E 00 | 0.100E 01 | 0.840E-01 |
| M974 8143 6 | 011 | 0.000E 00 | 0.100E 01 | 0.379E 03 |

The NWC site example (NA) contains only MUX data for the same time period. Type 3, channel 3, represents wind direction and has a value of 291.

Merged Hourly Average Files - 1 and 2 Hours - 80 Character, ASCII Record

One file has been generated for each episode for both time periods; each file contains merged ARB and NWC data, as well as Air Industrial Hygiene Laboratory (AIHL) filter chemistry data for both ARB and NWC sites. One record exists for every available parameter if any data exist for it during the specified time period, whether or not data exist for both sites; a flag is included in each record which indicates whether the record contains data from both sites, or only one site. These files contain not only averages for the time period, but also standard deviation values per parameter for each site for that period. Again, each record is self-identifying, by episode (A-L), date, and time. Time is identified by the begin hour of the averaging period. One record exists for each parameter having a value during the averaging period, and will contain both sites' data for that parameter, if available.

In addition to identifying a parameter by type and channel number, the mnemonic is also included. The available parameters, with corresponding channel numbers, are shown in Table A-4. The actual record format is defined in Table A-5.

The standard deviation values for AIHL data are actually the error value noted by AIHL. If a parameter is missing for one site, its average and standard deviation are set equal to zero.



Table A-4
HOUR AVERAGE FILES CHANNEL/MNEMONIC CORRESPONDENCE

| | Channel | Mnemonic | |
|--------|---|--|---|
| Type 3 | 1 2 3 4 5 7 8 9 11 12 13 14 15 16 17 20 21 22 23 24 | WDIR WSPD WSIG TOUT TIN BSCAT UVRAD BBRAD CNC 03 NO NO2 NOX RELHUM CO2 SO2 HCTOT CH4 CO C2H4 | |
| Type 4 | 25 1 2 3 4 5 6 7 8 9 10 11 12 22 23 24 25 26 27 28 29 30 | D = .0133 D = .0237 D = .0421 D = .0750 D = .133 D = .237 D = .365 D = .487 D = .750 D = 1.33 D = 2.37 D = 4.21 D = .0075 D = .0133 D = .0215 D = .0306 D = .0502 D = .0917 D = .149 D = .219 D = .306 | Electrical Aerosol Analyzer ARB Mobile Royco Optical Particle Counter Data Electrical Aerosol Analyzer NWC Mobile |

Table A-4 (Continued)

| | Channel | Mnemo | nic | |
|--------|---|---|------------|--|
| Type 5 | 0 0 | N S | | <pre>(northbound car count) (southbound car count)</pre> |
| Type 6 | (AIHL Respirable | ≘ Hi-Vol | (RH) Data) | |
| | 1 2 3 | NH4 NO3 SO4 | | (ammonium) (nitrate) (sulfate) |
| Type 7 | (AIHL NWC Total (TF) Data) | Filter, | Sequential | Sample (TFQ) and All Total Filter |
| | 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 | AS BRACRUFEA GG KAS MN NIB BS SSRTI V ZN | | <pre>(arsenic) (bromine) (calcium) (chromium) (copper) (iron) (gallium) (mercury) (potassium) (mass) (manganese) (nickel) (lead) (ribidium) (sulfur) (selenium) (sulfate) (strontium) (titanium) (vanadium) (zinc)</pre> |
| Type 8 | (AIHL ARB TFQ) | | | |
| | 1 2 3 4 5 | AS BR CA CR CU | | |

Table A-5
RECORD FORMAT, HOUR FILES

| Character | Identification | Possible Values | Format |
|-----------|-----------------|----------------------|--------|
| 1 | Site | A-L | A1 |
| 2-3 | Year | 74 | 12 |
| 4-5 | Month | 08,09 | 12 |
| 5-6 | Date | 14,5 | 12 |
| 8-9 | Hour | 06,19 | 12 |
| 10-11 | Minute | 00 | 12 |
| 12-13 | Type | 3 - MUX | |
| | · . | 4 - Particle | |
| | | 5 - Traffic | |
| | | 6 - AIHL RH | |
| | | 7 - AIHL TF, TFQ NWO | 3 |
| | | 8 - AIHL TFQ, ARB | _ |
| 14-15 | Channel | 1-30 | I2 |
| 16-23 | Mnemonic | see above (Table A-4 | |
| 24-33 | ARB Average | | E10.3 |
| 34-43 | ARB Standard De | viation | E10.3 |
| 44-53 | NWC Average | | E10.3 |
| 54-63 | NWC Standard De | | E10.3 |
| 64-65 | Merge Flag | -1:only Navy data | I2 |
| | | 0:data from both s | ites |
| CC 00 | DJ I | 1:only ARB data | |
| 66-80 | Blank | | |
| | | | |

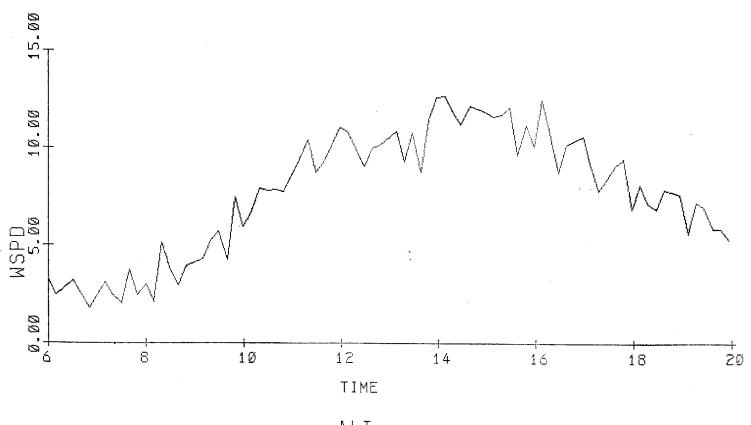
Following is an example of records from a 2-hour average file. The first record indicates that for episode A, which occurred 8-14-74, at time 0600 (for the period 0600 to 0759), type 3 data for channel 1 (wind direction), had the average value of 297°, with standard deviation of 153° for the ARB site, and had the average value of 150° and standard deviation of 130° for the NWC site. The flag (0) indicates that data is present for at least one 10-minute value during the 2-hour period for both sites. The flag (1) for inside temperature (TIN) shows that data was present only for the ARB site, while for CNC the flag (-1) indicates only the Navy site had data. The data occurs in order by type (3-8) and by channel number within type.

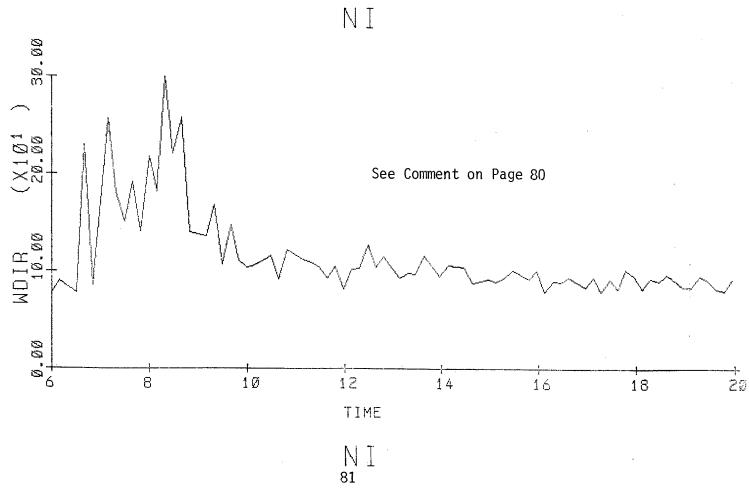
| A74 814 5 2 | 3 IWDIR | 0.297E 03 | 0.153E 03 | 0.1505.03 | 0.130E 03 8 | ā |
|-------------|-----------|-----------|-----------|-----------|-------------------|----------|
| A74 814 6 8 | 3 2WSPD | | | | 0.158E 01 0 | |
| A74 814 6 0 | | 0.494E 81 | | | 2.1002 21 | i |
| 874 814 5 0 | | | | 0 2005 02 | 9.828E-01 6 | a T |
| 974 814 5 9 | | | 0.755E 98 | 0.2021 02 | a.ovoc_01 6 | 4 |
| | | | | A 400E A. | 0 5015 00 0 | <u>:</u> |
| 974 814 6 0 | | | | 9.46ZE 01 | 0.5015 00 | ا ا |
| A74 814 6 0 | | 8.146F-82 | | | | 1 |
| ค74 814 5 8 | | 0.25iE-01 | 0.2646-01 | | | ĺ |
| A74 814 5 Ü | | | | 0.154E 98 | 0.517E 07- | 1 |
| A74 814 6 0 | 31203 | 0.397E-01 | 0.5056-02 | 0.398E-03 | 0.765E-03 0 | 3 |
| A74 814 6 8 | 313NO | 0.447E-02 | 0.6056-02 | 0.2605 00 | 9.101E 00 0 | 3 |
| A74 814 6 8 | 314H02 | 0.193E-01 | 0.700E-02 | | | 1 |
| 974 814 6 0 | 315NOX | 0.224E-01 | 0.121E-01 | 0.319E 00 | 8.123E 00 0 | 7 |
| A74 814 6 0 | 316RELHUM | | | | 0.484E-03 8 | |
| A74 814 6 8 | | | | | 0.281E 02- | |
| A74 814 6 đ | | 0.117E-01 | 0.181E-02 | | | í |
| | | 0.24GE 81 | | | | 4 |
| ค74 814 6 8 | | 0.205E 01 | | | • | 1 |
| A74 814 6 8 | | | | 0 7005 01 | 0.148E 01 8 | 1 |
| 974 814 6 8 | | | | a.330c al | 0.140E 01 8 | 3 |
| | | 0.133E 00 | | | • | Ĺ |
| 974 814 6 9 | | 0.891E 05 | | | | 1 |
| A74 814 5 8 | | 0.195E 05 | | | | 1 |
| A74 814 6 0 | | 0.491E 04 | | | • • | 1 |
| A74 814 6 0 | | 0.310E 04 | 0.343E 03 | | • | 1 |
| A74 814 6 0 | 4 5D=.133 | 0.136E 04 | | | • | 1 |
| 874 814 6 0 | 4 GD=.237 | 0.586E 03 | 0.367E 02 | | | 1 |
| A74 814 6 8 | 4 7D=.365 | 0.134E 03 | 0.958E 01 | | | 1 |
| A74 814 6 8 | 4 SD=.487 | 0.174E 03 | 0,229E 02 | | | İ |
| A74 814 6 0 | 4 9D=.750 | 0.9555 02 | 0.1495 02 | | | 1 |
| | | 0.473E 01 | | | | ļ |
| 974 814 6 9 | | 0.276E 00 | | | | i |
| A74 814 6 8 | | 0.142E 83 | | | | 1 |
| A74 814 6 0 | | | | 0 CADE 0: | 0.648E 00 0 | |
| A74 814 5 0 | | | | | | |
| | | | | | 0.194E 00 8 | |
| 074 814 6 0 | | | | | 0.137E 01 0 | |
| A74 814 5 0 | | | · · | | 0.000E 00 0 | |
| A74 814 6 8 | | | | | 0.700E-01 0 | |
| A74 814 6 0 | | | | | 0.400E-01 0 | |
| A74 814 6 0 | | | | | 0.800E-02 8 | |
| 974 814 6 0 | | 0.310E-01 | 0.300E-02 | 0.270E-01 | 0.3005-02 6 | ĵ |
| A74 814 S B | 7 6FE | 0.854E 89 | 0.3405-01 | 0.5568 00 | 0.220E-01 8 | 3 |
| 974 814 6 0 | 7 7GA | 0.900E-02 | 0.003E 00 | 0.140E-01 | 0.000E 00 8 | 3 |
| 974 814 6 8 | 7 8HG | 0.120E-01 | 0.009E 00 | 0.1405-01 | 0.000E 00 0 | 3 |
| A74 814 6 8 | 7 9K | 0.440E 00 | 9.7906-01 | 0.140E 00 | 0.600E-01 8 | ð |
| A74 814 6-8 | 710MAS | 0.752E 02 | | | | 1 |
| | | | | 0.1705-01 | 8.8885 8 8 | |
| 474 814 6 9 | | | | | 0.3005-02 | |
| 974 814 5 5 | | | | | 0.220E 30 0 | |
| 874 814 5 0 | 71278 | 0.1505_61 | 0.000E 01 | а 1907-01 | 0.220C 30 0 | اد ج |
| 474 Sid 5 3 | | | | | 0.000E 00 8 | |
| | | | | | | |
| | | | | | 0.300E-02 0 | |
| | 717804 | | | | | |
| 974 814 6 5 | | | | | 0.900E 00 9 | |
| 974 F14 S B | 719TI | U.570E-01 | ы.400E-01 | U.430E-01 | 0.3605-01 (| 3 |
| | | | | | | |



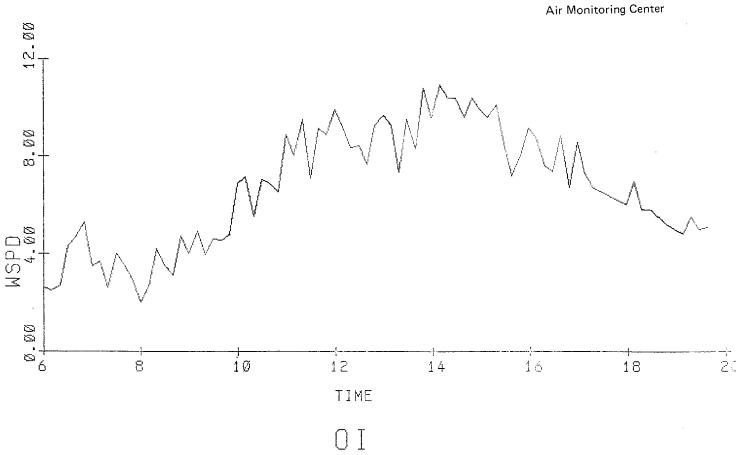
The remaining pages in Appendix A contain plots of the 10-minute data from sampling Day I, 30 August 1974. This day was selected because it is reasonably representative. The plots are presented so that the reader can gain a visual impression of the data.

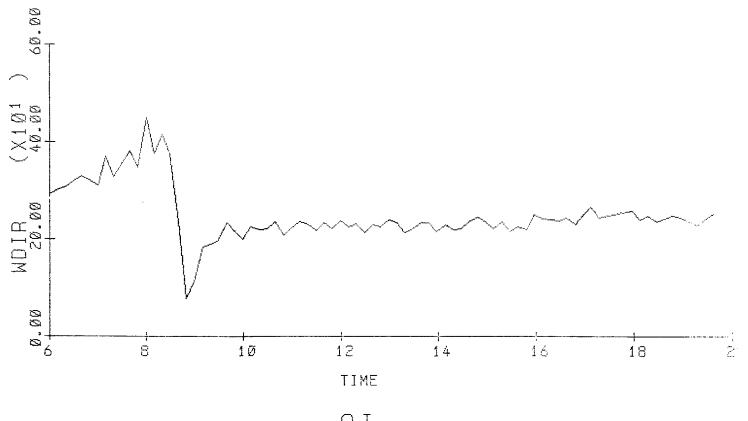
It is important to note that these plots were prepared to assist in the editing of the data, and therefore may contain some data points which were later classified as invalid and deleted. For example, the NI wind direction data were in error by a constant angle, and were corrected before inclusion in the data base. Therefore, for specific data, it is recommended that the data base itself be referred to. The units used for each measured quantity are specified in Table A-1 on page 62. The power of ten on some ordinates is the factor by which the numbers on the ordinate should be multiplied.



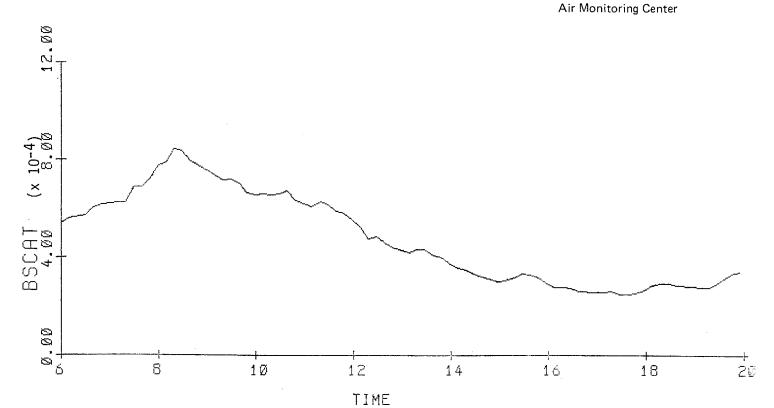


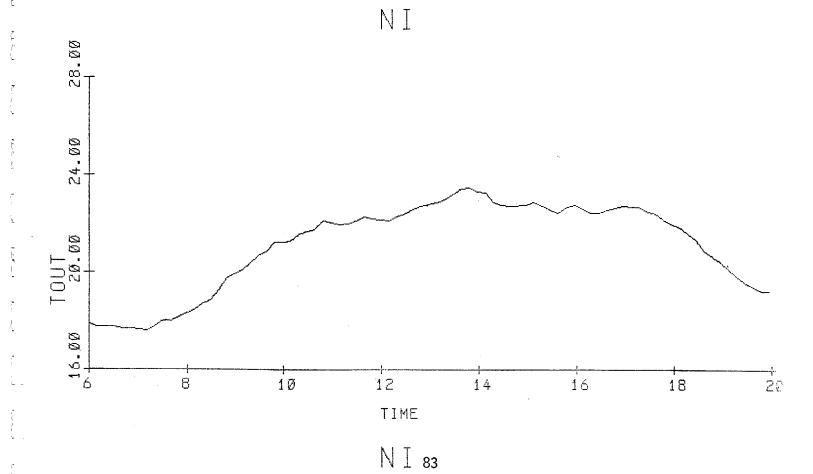




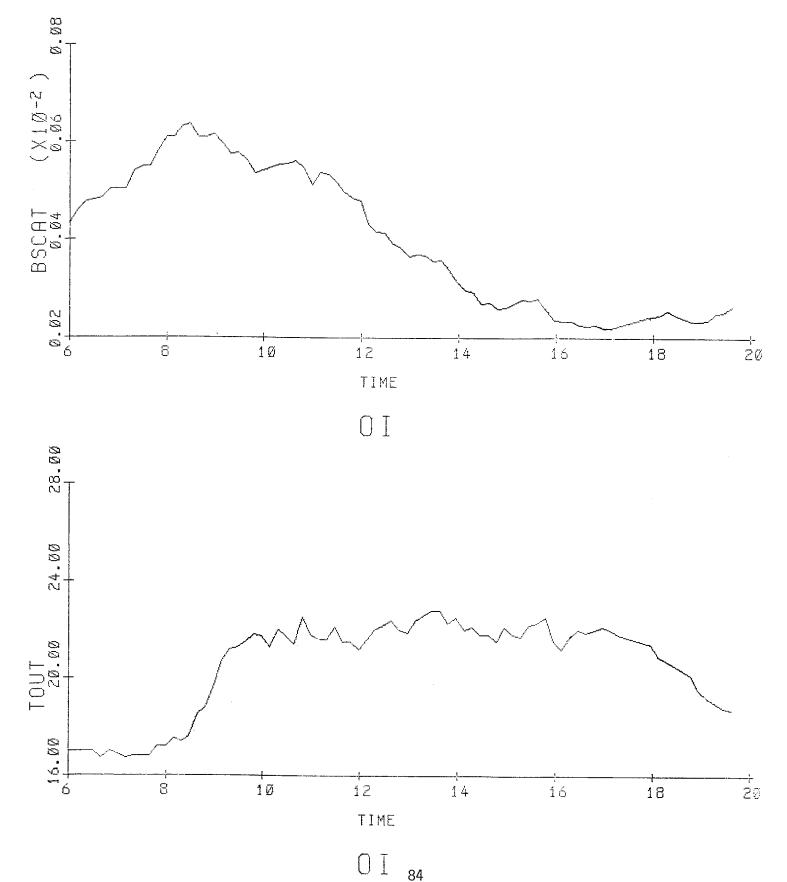






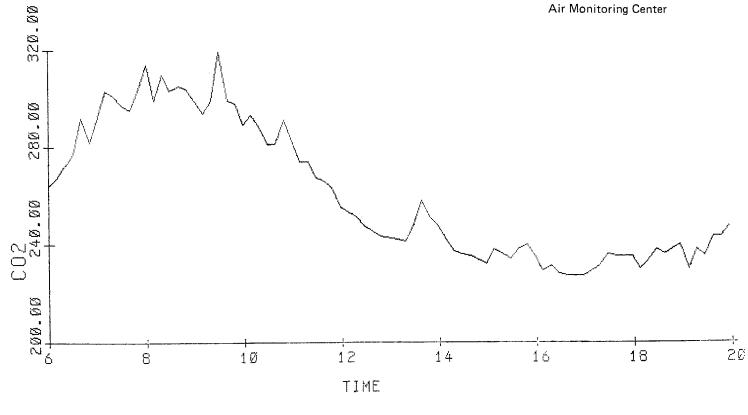


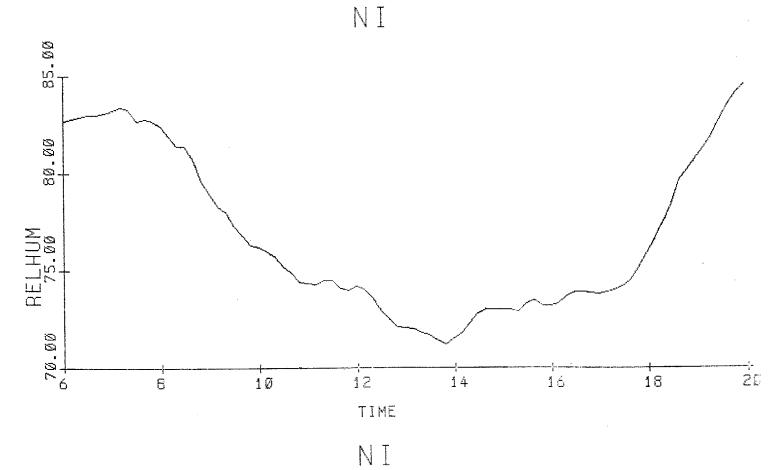






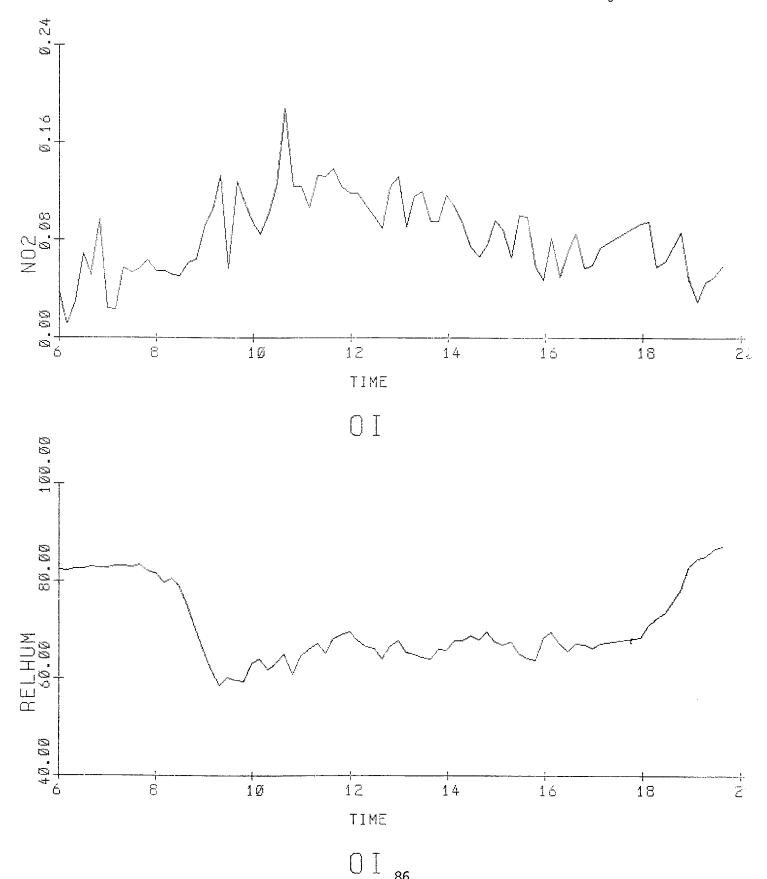
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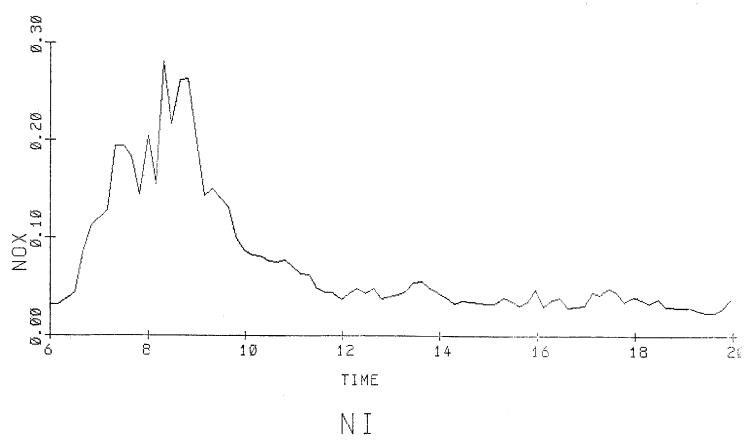


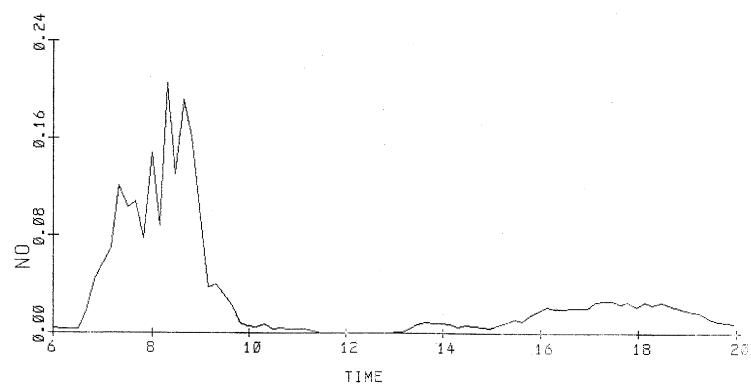


85

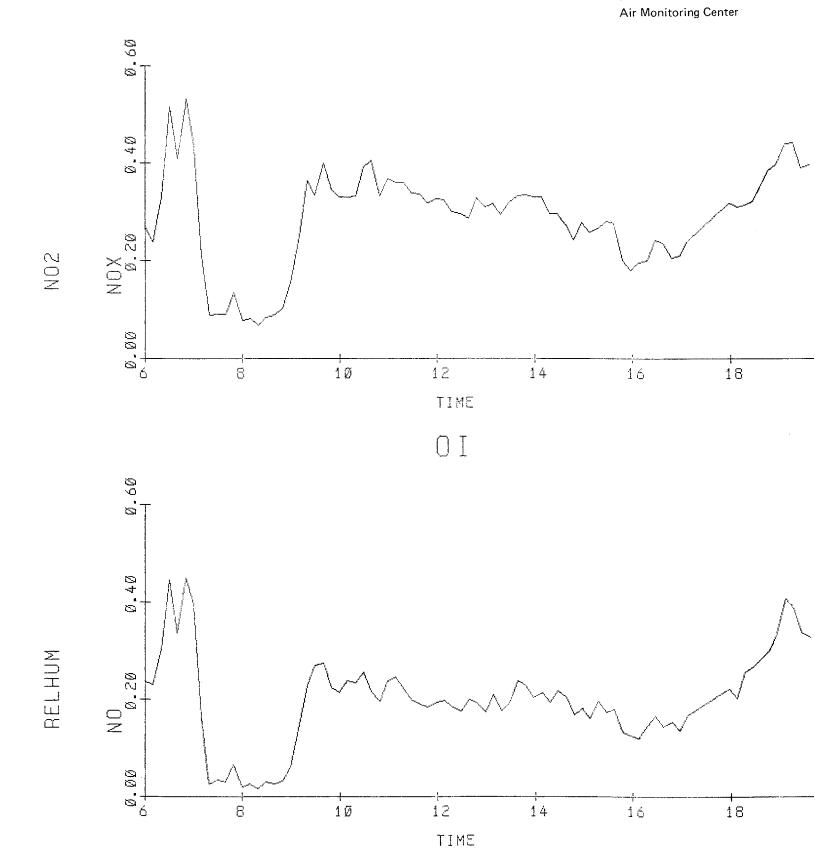




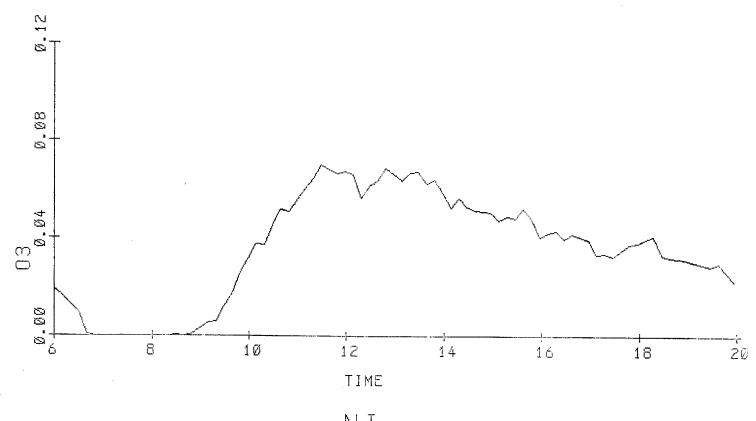


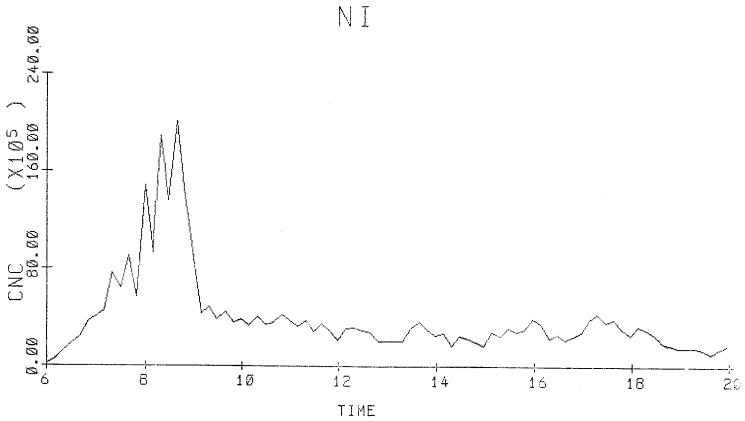


N I 87



O I₈₈

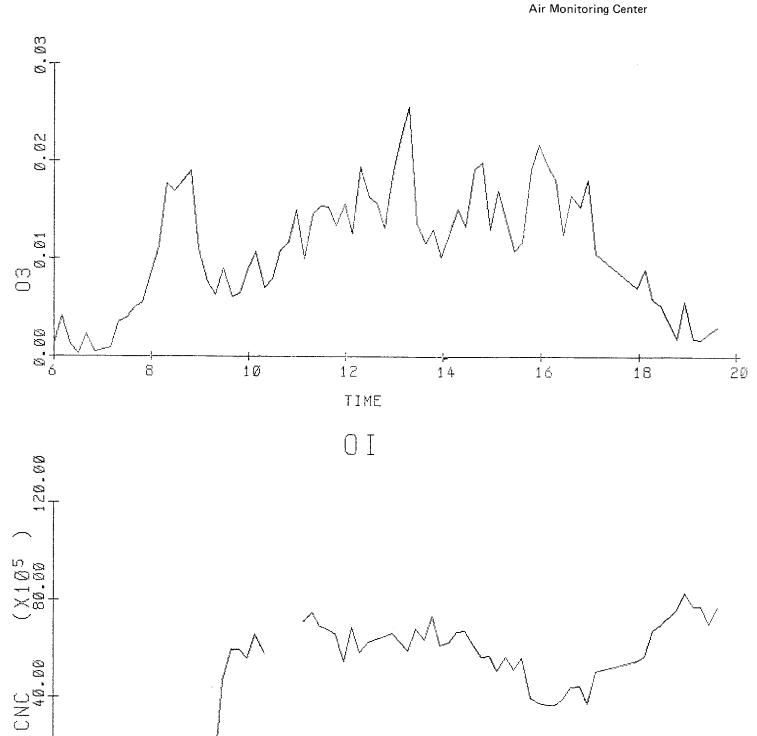




NI 89



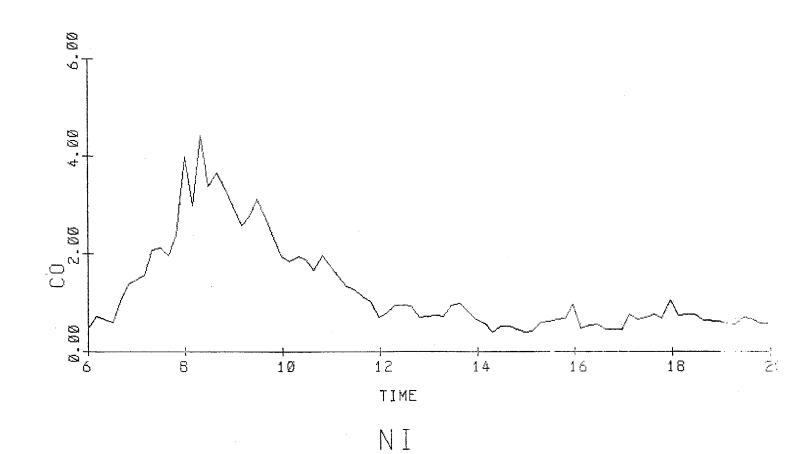
-i-

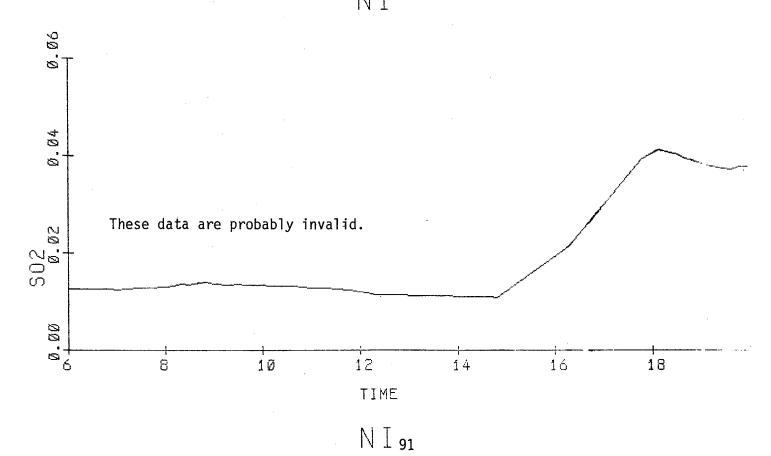


O I 90

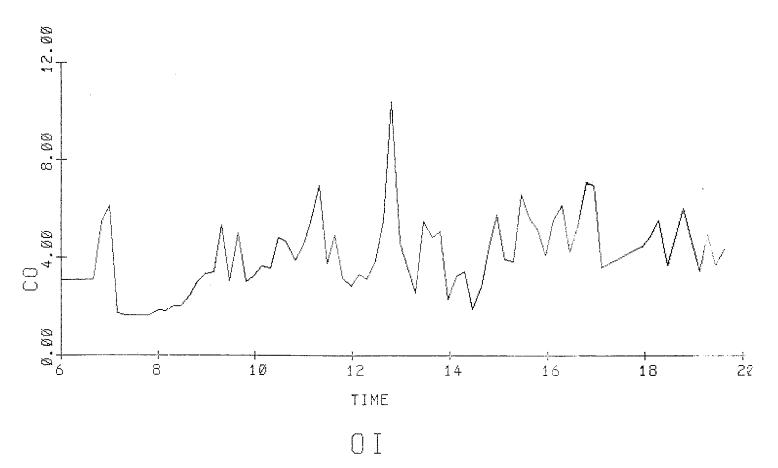
TIME

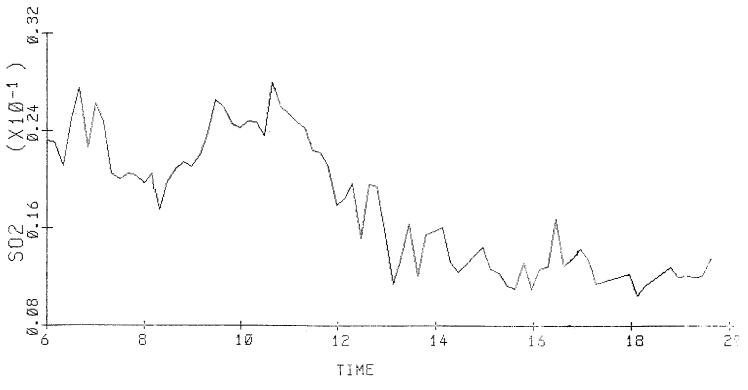
00.00













APPENDIX B

TWO-HOUR AVERAGE CONCENTRATION DIFFERENCES

ACROSS THE FREEWAY, AND

NORMALIZED CONCENTRATION DIFFERENCES



The following tables give two-hour average concentration differences across the freeway determined by both the continuous gas analyzers and by analysis of the two-hour filter samples. These tables were constructed to allow the combination and direct comparison of the continuous monitor and filter sample data. As explained in Section 6.3, normalized concentration differences were also calculated by dividing the observed concentration difference by the corresponding NO_X concentration differences. The purpose of this was to remove the effects of meteorology, sampling site location, and traffic density from the data, to produce direct information on the relative amounts of each of the pollutants emitted. In the following tables, the numbers appear in pairs. The top number is the concentration difference in the indicated units, and the one beneath it is the normalized difference.

The two right hand columns of the tables contain the mean and standard deviation of the four data points from the sampling periods beginning at 1200, 1400, 1600 and 1800 hr. Similarly, the bottom two rows of the tables give the mean and standard deviation of the data from all sampling days collected at the given time of day.

The last two columns in the next to the bottom row give the mean and standard deviation of the means over all sampling days for the afternoon sampling periods. This grand mean is a number frequently referred to in the body of the report. The last two columns in the bottom row give the mean and standard deviation of the standard deviations, and are of little significance. They appear here because they do no harm, and it would have taken additional programming effort to omit the calculation of these elements of the matrix.

Tables have not been included for As, Cr, Ga, Hg, Rb, Se, Sr, and V, because their concentrations were usually below the limit of detection. Also, data have been deleted from the tables for Ca, Cu, Mn, and Ti when one of the two values from which the concentration difference is calculated was below the limit of detection. In cases where data were deleted, the calculated means and standard deviations are not correct because the deleted data were included in the tabulated means and standard deviations.



No electrical aerosol analyzer data were included in these tabulations of differences because the particle size corresponding to the instrument channel boundaries were not the same for the Model 3030 on the west side and the Model 3000 on the east side of the freeway.

Except for the NO_X data, which come first because of their use in the normalization, the data are arranged in alphabetical order of the chemical symbol or mnemonic of the species. The optical particle counter data appear last in the tables. The tables are followed by plots of the one-hour average traffic counts in units of 100 vehicles/hour for both the northbound (N) and southbound (S) lanes. The days are identified by the code in Table 5-3.

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Air Monitoring Center

| STD DEV | 00 0.39E-01 | 00 · 0,11E 00 | 00 0.46E-01 | 00 0.57E-01 | 0 0.60E-01 | 0 0.57E=01 | 0 0,498-01 | 00 0.50E-01 | 0 0.69E-01 | 00 0.15E-02 | 00 0.51E-01 | 0 0.64E=01 | 00 0.48E-01 | 1 0,16E-01 |
|------------------------------|-----------------------|-----------------------|----------------------|----------------------|-----------------------|-----------------------|-----------------------|-----------------------|----------------------|-----------------------|-----------------------|-----------------------|-----------------------|----------------------|
| 12-18 | 01 0.00E 00 | 01 0,00E 00 | 01 0.00E 00 | 01 0.00E 00 | 1 0.00E 00 | 1 0.00E 00 | 1 0,00E 00 | 01 0.00E 00 | 1 0.00E 00 | 01 0.00E 00 | 01 0.00E 00 | 1 0.00E 00 | 01 0.00E 00 | 0 0,00E 00 |
| ME.AN 12-18 | 0.23E 0 0.10E 0 | 0.21E 0 0.10E 0 | 0.26E 0 | 0.28E 0 | 0.25E 0 0.10E 0 | 0.23E 0 | 0.268 0 | 0.23E 0 | 0.26E 0 | 0,21E 0 0,10E 0 | 0.17E 0 | 0.17E 0 | 0,23E 0 | 0.46E-01 0.00E 00 |
| * 30 | 0.26E 00 | 0,31E 00 | 0,31E 00 | 0,33E 00 | 0,33E 00 | 0,29E 00 | 0.33E 00 | 0,29E 00 | 0,34E 00 | 0.21E 00 | 0.23E 00 | 0.26E 00 | 0.29E 00 | 0.42E-01 |
| | 0.10E 01 | 0,10E 01 | 0,10E 01 | 0,10E 01 | 0,10E 01 | 0,10E 01 | 0.10E 01 | 0,10E 01 | 0,10E 01 | 0.10E 01 | 0.10E 01 | 0.10E 01 | 0.10E 01 | 0.00E 00 |
| • • • | 0.17E 00 | 0,21E 00 | 0.20E 00 | 0.20E 00 | 0.18E 00 | 0.18E 00 | 0,22£ 00 | 0.17E 00 | 0,17E 00 | 0,21E 00 | 0.11E 00 | 0.13E 00 | 0.18E 00 | 0,34E-01 |
| | 0.10E 01 | 0,10E 01 | 0.10E 01 | 0.10E 01 | 0.10E 01 | 0.10E 01 | 0,10ë 01 | 0.10E 01 | 0,10E 01 | 0,10E 01 | 0.10E 01 | 0.10E 01 | 0.10E 01 | 0,00E 00 |
| , | 0,25E 00 | 0,25E 00 | 0,27E 00 | 0,30£ 00 | 0,25E 00 | 0,26E 00 | 0.27E 00 | 0.24E 00 | 0.24E 00 | 0,22E 00 | 0.18E 00 | 0,17E 00 | 0.24E 00 | 0.38E-01 |
| , 41 | 0,10E 01 | 0,10E 01 | 0,10E 01 | 0,10E 01 | 0,10E 01 | 0,10E 01 | 0.10E 01 | 0.10E 01 | 0.10E 01 | 0,10E 01 | | 0,10E 01 | 0.10E 01 | 0.00E 00 |
| HUUR PST . | 0.25E 00 | 0.55E-01 | 0.24E 00 | 0,31E 00 | 0.23E 00 | 0.18E 00 | 0.23E 00 | 0,23E 00 | 0.27E 00 | 0.21E 00 | 0,15E 00 | 0.13E 00 | 0.21E 00 | 0,69E-01 |
| | 0.10E 01 | 0.10E 01 | 0.10E 01 | 0,10E 01 | 0.10E 01 | 0.10E 01 | 0.10E 01 | 0,10E 01 | 0.10E 01 | 0.10E 01 | 0,10E 01 | 0.10E 01 | 0.10E 01 | 0,00E 00 |
| | 0,25E 00 | -0.14E 00 | 0,24E 00 | 0,33E 00 | 0,18E 00 | 0.19E 00 | 0,15E 00 | 0.21E 00 | 0.28E 00 | 0.22E 00 | 0,16E 00 | 0.76E-01 | 0,18E 00 | 0.12E 00 |
| | 0,10E 01 | 0.10£ 01 | 0,10E 01 | 0,10E 01 | 0,10E 01 | 0.10E 01 | 0,10E 01 | 0.10E 01 | 0.10E 01 | 0.10E 01 | 0,10E 01 | 0.10E 01 | 0,10E 01 | 0.00E 00 |
| ; ; ; » | -0.12E 00 0.10E 01 | .0.21E 00 0.10E 01 | 0,30E 00 0,10E 01 | 0.31E 00 0.10E 01 | -0,25E 00 0,10E 01 | -0.99E-01 0.10E 01 | -0.83E-01 0.10E 01 | -0.80E-01 0.10E 01 | 0.10E-01 0.10E 01 | 0.66E-01 0.10E 01 | 0.15E-61 0.10E 01 | -0.26E 00 0.10E 01 | -0.32E-01 0.10E 01 | 0.19k 00 U.00E 00 |
| ; ; ; 9 | -0,30E 00 0,10E 01 | -0.83E-01 0.10E 01 | 0.28E 00 0.10E 01 | 0,33E 0U 0,10E 01 | -0.12E 00 0.10E 01 | -0.18E 00 | -0.20E 00 0.10E 01 | -0.11E-01 0.10E 01 | 0,16E 00 0,10E 01 | -0,38E 00 0,10E 01 | -0.37E 00 0.10E 01 | -0,51E 00 0,10E 01 | -0.12E 00 0.10E 01 | 0.27E 00 0.00E 00 |
| 10N E.S | /w0x | /NUX | /NUX | ZNUX | /אטא/ | /N0X | XDN/ | /NUX | ZNUZ | /NUX | /NUX | /NUX | /NUX | /wnx |
| CUNCENTRATION DIFFERENCES | RUX | NOX | NOX | NUX | NOX | X D N | NOX NOX | NOX | NOX | NOX | NOX | N C X | NUX ROX | XUN VE |
| DAY | Ą | ю | ၁ | a | . 20 | <u>.</u> | 9 | æ | - | 7 | ¥ | ٦ | พธาน | STO DEV |

TABULATION OF DIFFERENCES AND MURMALIZED DIFFERFINCES BY SPECIES

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Air Monitoring Center

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| | | : - | TABULATION OF | | DIFFERENCES AND NURMALIZED DIFFERENCES | JEED DIFFE | ЯΧ | SPECIES | | |
|---------------------------------------|-------------|------------------|-----------------|-----------------|--|-----------------|----------------|-----------------|-----------------|---|
| CUNCENTRATION DIFFERENCES | T10N CES | ; ; 4 | ; ; ; | HO | HOUR PST - | 1 4, | 16 | 18 | MEAN 12-18 | S |
| 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 | ZNOX | -1,500 | -0.175 1.520 | 3.260 13.100 | 2.600 | 2.280 9.050 | 1.440 8.280 | 3.410 13.300 | 2,433 10,258 | |
| # # # # | /NOX | -0.612 7.390 | -2.010 9.660 | -1.240 9.190 | 1.170 | 2,940 11,600 | 1.710 8.220 | 4.190 13.300 | 2,503 13,605 | |
| BR | XINI | 4.030 | 4.070 | 3,340 13,700 | 2.990 | 2.140 7.930 | 1.710 8.380 | 3.270 | 2.528 | |
| BR BR | /NUX | 3.730 | 3,480 11,300 | 3,520 | 2.830 | 2.660 8.840 | 1.270 | 2,850 8,690 | 2,403 8,260 | |
| BR BR | /nux | -0.418 3.370 | -1.080 | 2,500 | 2.630 | 2.140 8.530 | 1.570 | 3,820 11,700 | 2.540 10.075 | |
| BR BR | /NOX | -1.800 9.890 | -0.450 4.550 | 3.060 | 3,350 | 2,980 | 1,660 | 3,500 12,200 | 2,872 | |
| 8 R B R | /NOX | -1,390 | -0.240 | 2.050 | 2.980 | 2.800 | 1.880 | 4.030 | 2,923 10,968 | |
| BR BR | /NOX | -0.656 59,600 | 1.000 | 2.850 | 2.580 | 2.170 9.190 | 1.600 | 3,440 11,900 | 2.447 | |
| BR | XON/ | 2.630 | 000*99 | 3.780 | 2.890 | 2.790 | 1.820 | 4.250 | 2,938 11,350 | |
| 3 3 3 3 3 | ZRUX | 10.100 | 1.820 | 3,460 16,000 | 3,340 15,800 | 3.260 | 1.930 9.100 | 000.0 | 2.843 | |
| 8 K | ZNOX | -3.540 9.570 | 1,070 | 3.190 | 2,970 | 2.600 | 1,460 | 2.850 | 2.470 | |
| ## ## ### | ZNOX | -4.220 8.270 | -1.740 6.740 | 1.930 | 2.640 | 2,930 | 1.460 | 2.170 8.280 | 2.300 | |
| 88 84 84 | /hOx | -0.634 13.452 | 0,444 18,361 | 2,642 | 2.748 14.572 | 2.641 | 1.626 9.318 | 3,435 | 2.612 | |
| DEV BK BR | /N0X | 2.794 | 1.901 | 1.351 | 0,561 | 9.378 2.980 | 0.198 | 0.637 | 0,444 | |

0.837

0.882

1.347 5.548 0,727



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|------------------------------|----------------|----------------|----------------|--|----------------|-----------------|----------------|-----------------|----------------|----------------|----------------|-------|------------------------|----------------|
| STD DEV 12-18 | 0.304 | 0.189 4.535 | 0.070 | $\begin{pmatrix} 0.181 \\ 0.534 \end{pmatrix}$ | 0.416 | 0.200 | 0.136 0.603 | 0.105 0.456 | 0.100 | 0,309 1,445 | 0.188 1.419 | 0.104 | 0.151 | 0.051 |
| MEAN 12-18 | 0.405 | 0.278 | 0,310 | $\begin{pmatrix} 0.320 \\ 1.105 \end{pmatrix}$ | 0,382 | 0.223 | 0.238 | 0.278 | 0.305 | 0.557 | 0.400 | 0.214 | 0.318 | 0.156 1.138 |
| * 30 | 0.100 | 0.150 | 0,260 0,828 | 0.180 0.549 | 0.030 | -0.020 | 0.230 0.695 | 0.180 | 0,340 | 000.0 | 0,430 | 0.110 | 0.181 0.626 | 0.131 0.518 |
| 1 9 1 | 0,190 1,090 | 0.150 | 0.360 | | 0.160 0.884 | 0.140 | 0.090 | 0.200 | 0.430 | 0.200 0.943 | 0.340 | 0.150 | $\binom{0.213}{1.279}$ | (0.105) |
| 1 4 | 0.630 | 0,250 | 0.240 | 0.450 | 0.370 | 0,360 | 0.210 | 0.400 1.690 | 0.240 0.996 | 0.730 | 080*1 | 0,340 | 0.368 1.558 | 0.168 |
| HOUR PSI - | 0./00 2.810 | 0,550 | 0.380 | 0.500 | 0.970 | 0,410 | 0.420 | 0.330 | 0.210 | 0.740 3.490 | 0.640 4.300 | 0.254 | 0.509 | 0.222 |
| 10 HOU | 0,550 2,210 | 0,260 | 0.510 | 0.410 | 0.970 | 0,710 3,800 | 0.360 2.340 | 0,490 | 0.490 | 0.380 | 0.720 | 0,210 | 0,505 | 0.213 1.808 |
| ; | 0.460 | 0.310 | 0,860 | 0,600 | 0.280 | 0.430 | 0,380 | 0.450 | 0.420 | 0.790 | 0.890 | 0.260 | 0.511 7.992 | 0,223 |
| ; ; ; q | 0.210 | 0,340 | 0.570 | 0.310 | 0.180 | -0.110 0.604 | 0.270 | -0.020 1.820 | 0.210 | 0,130 | 0.970 | 0,650 | 0.309 | 0.298 1.854 |
| 10N ES | /и0х | ZNOX | ZNOX | /NOX | / NOX | ZNOZ | /NUX | /NOX | ZNDX | /NO./ | /NUX | YOUZ | X D N N | 7.40% |
| CONCENTRATION DIFFERENCES | CA | CA | CA | CA | CA | CCA | CA | CA | CCA | 0 0 0 | CA | CA | CA | EV CA |
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| > - | CONCENTRATION DIFFERENCES | 83 83 | • | 1 30 | . 01 | HOUR PST - | 1 47 | 101 | 18 | HEAN 12-18 | STD DEV 12-18 |
|---------------|------------------------------|----------|------------------------|------------------------|------------------------|----------------------|----------------------|------------------------|----------------------|--|----------------------|
| | CNC | /NUX | | | 0.85E 05 0.34E 07 | 0,21E 0/ 0,85E 07 | 0,21E 07 0,84E 07 | 0.30E 07 0.17E 08 | 0.57E 07 0.22E 08 | $\begin{pmatrix} 0.32E & 07 \\ 0.14E & 08 \end{pmatrix}$ | (0.17E 07) |
| | CNC | ZNOX | -0.10E 06 0.12E 07 | 0.14E 05 +0.67E 05 | -0.17E 06 0.57E 07 | 0.87E 06 0.16E 08 | 0,34E 06 0,13E 07 | -0.19E 06 -0.92E 06 | 0.11E 07 0.34E 07 | 0,52E 06 0,49E 07 | 0.57E 06 |
| | CNC | ZNOX | 0.12E 07 0.42E 07 | 0.51E 06 0.20E 07 | -0.28E 06 | -0.11£ 07 | -0.68E 06 | -0,16E 07 | -0.13E 07 | -0.12E 07 | 0.40E 06 0.23E 07 |
| | CNC | XONZ | -0.55E 06 -0.17E 07 | -0.10E 07 | 0.15E 07 0.47E 07 | 0.22E 07 0.72E 07 | 0.19E 07 | 0,30E 07 0,15E 08 | -0.50E 05 | 0,18E 07 0,71E 07 | 0.13E 07 0.61E 07 |
| | CNC | XON/ | 80 308°0 0.808 07 | -0.15E 08 0.61E 08 | 0,29E 07 0,16E 08 | 0,59E 07 0,25E 08 | 0.50E 07 | 0,26E 07 0,15E 08 | 0.61E 07 0.19E 08 | 0,49E 07 | 0.16E 07 0.45E 07 |
| | ONO | ZNUX | | | | | | | | | |
| | CNC | XNNX | | | | | | | | | |
| | CNC | ZHOX | -0.70E 07 0.64E 09 | -0.12E 08 | 0.83E 06 0.39E 07 | 0,19E 07 0,84E 07 | 0.00E 00 | 0.45E 06 0.27E 07 | 0.40E 07 0.14E 08 | 0,21E 07 0,83E 07 | 0.18E 07 |
| | CNC | ZNOX | -0.32E 07 | -0.81E 07 | 0.24E 07 0.84E 07 | 0,36E 07 0,14E 08 | 0,32E 07 0,13E 08 | 0.84E 06 0.48E 07 | 0.51E 07 0.15E 08 | 0,32E 07 0,12E 08 | 0.18E 07 0.47E 07 |
| | CNC | XON/ | -0.22E 08 | -0.77E 07 -0.12E 09 | 0,69E 06 0,32E 07 | 0.31E 07 0.15E 08 | 0.36E 07 0.17E 08 | 0,16E 07 0,75E 07 | 0.74E 06 0.35E 07 | 0.23E 07 0.11E 08 | 0,13E 07 0,62E 07 |
| | CNC | ZNOX | -0.27E 08 | -0,64E 07 | 0.11E 07 0.07E 07 | 0,30E 07 0,20E 08 | 0.37E 07 0.21E 08 | 0,10E 07 0,98E 07 | 0.77E 06 0.34E 07 | 0.21E 07 0.14E 08 | 0.14E 07 0.85E 07 |
| | CNC | /h0x | -0.25E 08 0.50E 08 | -0.17E 08 0.66E 08 | -0.25E 07 -0.33E 08 | 0,25E 07 | 0.31E 07 0.18E 08 | 0.35E 06 0.28E 07 | 0.32E 07 0.12E 08 | 0,23E 07 0,13E 08 | 0.13E 07 0.76E 07 |

TABULATION OF DIFFERENCES AND NURMALIZED DIFFERENCES BY SPECIES

| | STD DEV 12-18 | 0.572 | 0.828 4.981 | 0.797 3.952 | 0.982 | 0,887 | 1,517 | 1.570 | 0.872 5.360 | 0.523 | 0.508 2.450 | 0,911 | 0.599 | 0.760 | 0.155 |
|---|------------------------------|------------------|------------------|-----------------|-----------------|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|------------------|-----------------|-----------------|----------------|
| | MEAN 12-18 | 1.800 8.113 | 1,005 | 0.918 3.828 | 2.038 8.015 | 1.325 | 3,275 | 3,778 | 3,303 | 3,965 16,800 | 3.825 | 3,985 | 4,385 | 2.800 | 1.378 |
| SPECIES | * 8 | 2,320 9,030 | 1.300 | 0,980 | 2.130 | 1.050 | 2,900 | 3.880 11.700 | 3.710 | 3,860 11,400 | 3,630 | 3,380 14,800 | 4.180 | 2,777 | 1.182 4.878 |
| | 1 9 | 2.270 | 1.690 8.120 | 1.880 | 3,380 16,900 | 2,630 14,500 | 5.490 | 5.790 | 3.580 | 4.720 | 4.570 | 5.190 48.500 | 4.900 | 3.841 22.953 | 1.460 |
| DIFFERENCES AND NORMALIZED DIFFERENCES BY Cawhow Manovide | , , , , | 1,300 | 1,230 | 0,880 3,260 | 1,480 | 0.650 | 2.640 | 3,460 13,000 | 3.910 | 3.520 | 3,670 | 4.180 | 3.630 | 2,546 | 1.333 |
| ERENCES AND NURMALI | JR PST - 12 | 1.310 | -0.260 | -0.010 | 1.160 | 0.970 | 2.070 | 1,980 8,430 | 2.010 8.740 | 3,760 | 3,430 16,200 | 3.190 | 4.830 38.000 | 2.037 | 1,535 |
| DIFFERENCES | 10 1 HUUK | 0.780 | -1,040 | 1.840 | 1,020 | 0,960 | 3.220 | 2.210 | 2.260 | 2.780 | 3,410 15,800 | 3,890 | 2.940 38.700 | 1,863 | 1,621 |
| TABULATION OF | ; ; | -2,340 20,300 | -1.380 6.630 | 3,280 10,800 | 1.770 | -5.400 21.900 | 0,360 -3.640 | 0.200 | -0.520 6.500 | -0.190 | 1.630 | 1.620 108.000 | -0.220 | 0.099 | 2,259 |
| T. | • | -3.750 12.600 | -1.490 18.000 | 2,560 8,980 | 1.890 | -3.810 | -0.900 4.950 | -1.150 5.610 | 0.020 | 1.440 8.830 | -2.130 5.550 | -1,920 5,190 | -1.900 | -0.928 8.998 | 2.059 8.395 |
| | 8.3 NO.1 | /NUX | /nux | /n0x | / NUX | 7 NO X | /NUX | /NUX | XON/ | /NOX | /NUX | /NOX | /kux | ZNUX | ZNOX |
| | CONCENTRATION DIFFERENCES | 200 | 00 | 00 | 00 | 00 | 00 | ັດວ ດວ | 000 | 00 | იე | 00 | 00 | 00 | 0,0 0,0 |
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| STD DEV 12-18 | 0.018 | 0.021 | 0.034 0.131 | 0.018 | 0.020 | 0.030 | 0.025 | 0.013 0.039 | 0.020 | 0,005 | 660°0 600°0 | 0.031 | 0.005 | 0.007 |
|------------------------------|------------------|-----------------|----------------|----------------|------------------|------------------|------------------|-----------------|----------------|--------|------------------|--------|--------|---------|
| MEAN 12+18 | 0.012 | 8£0°0 000°0 | 0.020 | 0.015 0.058 | -0.018 | -0.014 | -0.005 | 0.018 | -0.004 | 0.035 | -0.023 | 0.024 | 0.004 | 0.026 |
| * & | -0.001 | -0.029 | 0.001 | 0.026 | -0.002 | -0.015 -0.052 | 0.001 | 0.034 | -0.009 | 0000.0 | -0.029 | 0.010 | -0.001 | 0.020 |
| 1 9 1 | 0.037 | 0.021 | -0.011 | 0.024 | -0.041 | -0.056 | -0.041 -0.185 | 0.008 | 0.019 | 0.036 | -0.032 | 0.053 | 0.001 | 0.036 |
| 1 4 4 | 0.001 | 0000.0 | 0.067 | 0.021 | -0.001 -0.004 | 0.009 | 0.004 | 0.008 | 0.002 0.008 | 0.039 | -0.016 | -0.012 | 0.010 | 0.023 |
| HUUK PSF - 12 | 0°00°0 6°0°0 | 0,008 0,145 | 0.021 | -0.012 | -0.027 | 0.007 | 0.018 | 0.022 | -0.028 | 0.029 | -0.014 -0.094 | 0.047 | 0.007 | 0.023 |
| . 01 | -0.051 -0.205 | -0.004 0.030 | -0.006 | 0.022 | 0.013 | -0.033 | -0.011 | 0.016 | 0.008 | 0.029 | 0.017 | 0.044 | 0.004 | 0.027 |
| 1 20 | 0.019 | 0.012 | 0.027 | 0.016 | .0.002 | 0.026 | 0.020 | 0.039 -0.488 | -0.033 | 0.041 | 0.001 | 0.005 | 0.014 | 0.020 |
| ! ! ! 9 | 0.004 | 0.035 | -0.001 | -0.009 | -0.020 | -0.045 0.247 | 0.038 | -0.005 0.455 | 0.035 | -0.020 | -0.007 0.019 | 0.023 | 0.002 | 0.026 |
| LES | ZhUX | XON/ | /NUX | ZNNZ | /NUX | ZNOX/ | /NOX | /NOX | /NOX | ZNDX | /NUX | ZNOZ | ZNUX | /NUX |
| CUNCENTRATION DIFFERENCES | 000 | no no | CO | CO | CU | no | n n O | ຄວ | CO | CO | 00 | ກວ | ກຸວ | EV CU |
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TABULATION OF DIFFERENCES AND NURMALIZED DIFFERENCES BY SPECIES

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| | STD DEV 12-18 | 0.466 1.758 | 0.427 | 0.166 | 0.261 | 0.518 | 0.305 | 0.184 | 0.308 1.348 | 0.057 | 0.835 3.903 | 0.786 5.500 | 0.23b 1.808 | 0.320 | 0.179 |
|----------------------------|------------------------------|----------------|----------------|------------------|----------------------|--------------------|----------------|----------------|----------------|----------------|----------------|-------------------|----------------------|------------------------|-----------------|
| | MEAN 12-18 | 0.638 2.662 | 0,556 | 0.497 | 0.642 | 0.661 2.828 | 0,330 1,598 | 0,306 | 0.395 | 0.542 | 1.348 6.323 | 0.947 | 0.4512.910 | 560°€ 585°0 | 9.332 |
| SPECIES | * 8 T | 0.200 | 0,419 | 0.516 | 0.407 | 0.213 0.653 | 0,160 | 0.441 1.330 | 0,320 | 0.499 | 0000.0 | 0.780 | 0.309 | 0,388 1,330 | 0.178 |
| ВΥ | 1 9 | 0.274 | 0.342 | 0.291 1.430 | 0.469 2.350 | 0,330 | 0.039 | 0.149 | 0.284 1.690 | 0.533 3.060 | U.385 1.820 | 0.704 | 0.193 | 0.333 2.031 | 0.177 |
| IZEO DIFFERENCES | ; ; ; | 0.989 3.920 | 0.273 | 0.484 | 0.712 | 0,741 | 0,387 | 0.145 | 0.136 | 0.625 2.590 | 1.810 8.420 | 0.236 | 0.657 3.860 | 0.600 | 0.464 |
| DIFFERENCES AND NORMALIZED | IR PST - | 1.090 4.380 | 1.190 | 0.696 2.880 | 0.979 3.170 | 1,360 5,890 | 0,733 | 0.488 | 0.841 3.660 | 0,512 1,920 | 1.850 | 2.070 | 0.644 | 1.038 | 0.508 5.822 |
| DIFFERENCES | - HUUR | 0.671 | 0.500 | 0,813 | 1,360 | 1,520 8,400 | 0.980 | 0.811 | 1.090 | 1.300 | 0.544 | 0.690 | 0.137 | 0.858 3.039 | 0.401 2.878 |
| TABULATION UP | 1 1 1 | 0.533 | 0.522 | 1,490 4,900 | 0.905 | 0.279 | 0.506 | 0.556 | 0.660 | 0,670 | 1.490 | 2,260 | 0.630 | 0.876 18.133 | 0.576 |
| JA | ! ! ! 9 | 0.298 | 0.474 | 0.629 | 0.677 | 0.346 | -0.170 | 0.764 | 0,110 | 0.577 3.540 | 0.310 | 1,020 | 1,240 | 0,523 | 0,386 3,771 |
| | LCN S.S | /hux | ZNOX | /NUX | / NUX | /NOX | /NUX | XNNZ | /NOX | /NUX | ZHUX | /NUX | ZNUX | /NUX | /bux |
| | CUNCENTRATION DIFFERENCES | ندا عن عدید | 77 77 71 73 | 22 (23 32 (22 | ज्या हो। इंग्रह्म | क्य क्य क्य क्य | 9 2 9 2 | না না ডে.ড. | ध्यं च भ क | ক ক ক স | क्र क क्रा | ज्यं जि कि.कि. | क्र क्र अस्त्रेची | ध्यं व्यं व्यः व्यः | a a a ≠ > |
| | C. DAY | æ | ಖ | O | ۵ | ند | ٠. | છ | Ξ | - | r | × | ے | MEAN | STD DEV |

| CO 7 | CONCENTRATION DIFFERENCES | TUN | , , , , | 1 1 50 | 1 0 | HOUR PST - | 1 4 | ; ; 9 | * 8 | MEAN 12-18 | STD DEV 12-18 |
|-------|------------------------------|--------|------------------|-----------------|-----------------|----------------|----------------|----------------|----------------|----------------|------------------|
| | GA GA | /NUX | 0.005 | 0.001 | 0.008 | 0.010 | 0,012 | 0.008 0.046 | 0.005 | 8£0°0 | 0.003 |
| | GA GA | XNN/ | 090.0 | -0.006 | -0.004 0.030 | 0.004 | 0.010 | 0.007 | 0.010 | 0.008 0.044 | 0.003 |
| | GA GA | /NOX | 0.012 | 0.013 | 0.012 | 0.015 0.062 | 0.004 | 0.012 0.059 | 0.011 | 0.010 | 0.005 |
| | GA GA | /NUX | 0,013 | 0.012 | 0.014 0.043 | 0,012 | 0,011 | 0.001 | 0,012 0,037 | 0.009 | 0.005 |
| | GA GA | X ON / | -0.005 | 0.005 | -0.001 | -0.001 | 0.010 | 0.000 | 0,010 | 0.007 | 0.005 |
| | GA GA | /NUX | \$60.0° | 000*0 | 0.009 | 0.012 | 0.009 | 0.007 | 0.010 | 0.010 | 0.002 |
| | . 64 6.8 | ZNUX | -0.007 0.034 | -0.001 0.012 | 0.006 0.039 | 0.001 | 0.009 0.034 | 0.008 | 0.012 | 0.008 | 0.005 |
| | 6.6 6.8 | XNOX | -0.004 0.354 | 000000 | 800°0 800°0 | 650.0 | 0.010 | 0.006 | 0.003 | 0.007 | 0.003 |
| | G G G A | XNOX | 0.006 | 0.003 | 0.016 | 0.010 | 0.010 | 0.012 | 0.015 0.044 | 0.012 | 0.002 |
| | GA | /NOX | .0.00/ 0.018 | 000.0 | 0.005 | 0,009 | 0.010 | 0.006 | 000.0 | 0.008 9.039 | 0.002 |
| | GA GA | XWX/ | -0.008 | 0.003 | 0.008 0.049 | 600°0 | 0,008 | 0.007 | 0.008 | 0.008 | 0.001 |
| | GA GA | Zh0X | -0.009 0.018 | -0.005 0.019 | 0.003 | 0.009 | 0.014 | 0.011 | 0.009 | 0.011 | 0.002 |
| Ą | G G | ZNUX | -0.002 0.060 | 0.002 | 0.007 0.037 | 0.008 | 0.010 | 0.008 | 0.010 | 0.009 | 0.001 0.006 |
| 0 UEV | GA GA | /NUX | 950°0 800°0 | 960.0 | 0.006 | 0.005 | 0.002 0.015 | 0.003 | 0.003 | 0.003 | 0.001 |

TABULATION OF DIFFERENCES AND NURNALIZED DIFFERENCES BY SPECIES

| | MEAN STD DEV 12-18 12-18 | 0,007 0,099 0,066 0,420 | 0.050 0.071 0.609 1.071 | 0.065 0.077 0.262 0.291 | 0.140 0.127 0.518 0.427 | 0.065 0.065 0.314 0.310 | 0.027 0.198 0.220 1.084 | 0,065 0,044 0,267 0,186 | 0.168 0.190 0.887 1.163 | 0.093 0.068 0.370 0.279 | 0,207 0,119 0,970 0,560 | 0.135 0.155 0.798 1.007 | 0.047 0.121 0.477 0.803 | 0.085 0.074 0.455 0.429 | 0.102 0.025 0.501 0.244 |
|------------------------|------------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| SPEC1ES | * 81 | 056.0- | 950°0 080°0 | -0,020 | -0.010 | -0,020 | -0.090 -0.314 | 0.010 | 0.060 | 0,050 | 000°0 | 0,190 | -0.100 | 0.001 | 0,084 0,338 |
| κ. Y | 1 97 | -0.345 | -0.040 | 0.020 0.098 | 0.140 | 0.120 0.663 | -0.100 | 0.100 | 0.430 | 0.030 | 0.070 | 0,010 | 0.120 | 0.070 | 0.137 |
| NURMALIZED DIFFERENCES | 1 5 1 | 0,060 | 0.040 0.354 | 0.140 | 0.130 | 0.110 | -0.020 | 0.100 | 0000.0 | 0.180 | 0.260 | 0.010 | 000.0 | 0.088 | 0.084 0.365 |
| ANO | HOUR PSI - | 0.120 | 0.120 | 0.120 | 0.300 | 0.050 | 0.320 1.820 | 0.050 | 0.180 | 0.110 | 0.290 | 0.330 | 0.170 | 0.180 | 0.104 |
| DIFFERENCES | 10 . HUI | 000.0 | 0.020 | 0.110 0.453 | 0.070 | 0.390 | 0.230 | 0,378 2,450 | 0.260 | 0.280 | 0.040 | 0.030 | -0.010 | 0.153 | 0.147 |
| IABULATIUM UF | 1 33 | 0.020 | 0.260 | 0.340 | 0.150 0.485 | 0.420 | 0.110 | 0.480 -5,780 | 0.200 | 0,180 | 0.360 | 0.600 | 0.370 | 0.288 4.288 | 0.174 |
| 1.8 | : : : | 0.300 | 0.290 | 0.14U 0.491 | 0.020 | 0.100 | 0.050 | 0.540 | 0.170 | 0.130 0.798 | 0.230 | 0.430 | 0.530 | 0,244 | 0,178 4,390 |
| | I I UN CES | /PUX | XD4/ | XU81 | /NUX | XON/ | /NUX/ | /nux | X00X | XNUX | ZnnX | 7 HUX | XUN/ | /nux | 71:0X |
| | CORCENTRALIUN DIFFERENCES | ጙ ጙ | ĸΧ | ×× | * * | ۷ × | * * | * * | * * | 4 K | ** | * * | * * | * * | 7 X X |
| | UAY | α | æ | ົບ | Ç. | यो | <u>.</u> | 9 | x | _ | 7 | × | ے | MEAN | STO DEV |

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|------------------------------|--------------------|--------------------|-------------------|-------------------|--------------------|-------------------|-------------------|---------------------|-------------------|-------------------|--------------------|-------------------|-------------------|--------------------|
| STD DEV 12-18 | 12.384 | 16.187 | 9.175 39.369 | 000.0 | 26.119 111.034 | 9,789 53,315 | 8.250 27.059 | 5.723 13.502 | 13.976 26.829 | 37,604 177,350 | 18.801 | 22,092 175,316 | 13.575 95.688 | 6.222 |
| MEAN 12-18 | 40,575 174,500 | 30.175 304.750 | 27.150 107.050 | 53,400 173,000 | 33,375 141,550 | 13.575 | 15.725 58.050 | 15.150 | 26.175 98.800 | 58.100 272.767 | 43,175 281,250 | 23.475 | 29.059 149.062 | 15.219 |
| * 80 | 30,600 | 17,200 54,600 | 23,700 | 000.0 | 9.800 30.100 | 5.000 | 24.100 72.800 | 21.100 72.800 | 46,800 138,000 | 000.0 | 32,400 142,000 | 19.100 72.900 | 22,980 79,510 | 11.855 |
| 1 9 1 | 30,300 | 18.600 89.400 | 17.900 | 000*0 | 13,600 | 5,400 29,700 | 5.100 | 8,200 48,800 | 15.800 | 20.200 95.300 | 30,700 | -4.800 | 14.636 | 10.764 |
| 1 4 | 45,700 181,000 | 32,900 130,000 | 27.400 101.000 | 000.0 | 46.100 184.000 | 20.100 75.800 | 13,800 | 18,300 77,500 | 21.500 | 58,700 | 38,700 220,000 | 32,300 190,000 | 32,318 143,018 | 13.914 |
| HOUK PSI - | 55.700 224.000 | 52.000 945.000 | 39.600 164.000 | 53,400 | 64,000 277,000 | 23,800 135,000 | 19.900 84.700 | 13.000 | 20.600 77.200 | 95,400 450,000 | 70,900 | 47.300 | 46,300 | 24,344 |
| 1 0 H | 45,700 184,000 | 15,300 | 26,200 108,000 | 46,900 143,000 | \$8,000 320,000 | 50,000 | 46.000 299.000 | 18,000 84,500 | 33.000 | 38.600 179.000 | 67,000 | 19,000 250,000 | 38.642 187.458 | 16,579 |
| 1 30 | 25,200 -219,000 | 17.100 -82.200 | 49,700 | 38.500 125.000 | 1,000 | 3,000 | 6.000 | -6,000 75,000 | -7.000 -7.000 | 53.300 808.000 | 80,000 5330,000 | 9,000 | 22,483 446,521 | 27,414 1574,487 |
| , , , | 0.00.0 | 15,700 -190,000 | 33,700 | 45,400 139,000 | -0.200 | -12.000 65.900 | 28.800 | -65,700 5970,000 | 13,000 | -18.900 49.200 | -2,000 5,410 | -7,000 13,700 | -0,264 571,038 | 29,341 1792,693 |
| 1UN ES | ZDVZ | XUUX | /NOX | /NUX | /n0x | /NOX | ZNUX | ZONZ | ZROX | ZNOX | ZONZ | /NUX | XNN/ | ZUNZ |
| CONCENTRALION DIFFERENCES | MAS | MAS | MAS | MAS | MAS MAS | MAS MAS | MAS MAS | MAS MAS | MAS | MAS | MAS | MAS | MAS | MAS |
| DAY | ۷ | r | U | a | ಎ | ī | و | r | - | 7 | × | ي. | MEAN | SIU UEV |

TABULATION OF DIFFERENCES AND NORMALIZED DIFFERENCES BY SPECIES

| STD DEV 12-18 | (0.007) | 0.015 | 0.009 | 0.008 | 0.012 | $\begin{pmatrix} 0.005 \\ 0.029 \end{pmatrix}$ | $\begin{pmatrix} 0.007\\ 0.029 \end{pmatrix}$ | 0.010 | (0.006) | 0.012 0.054 | 0.015 | 0.006 | 0.006 | 0,003 |
|---------------------------|-------------|----------------|----------------|----------------|---------------|--|---|------------------|----------------|----------------|------------------|--------|--|--|
| MEAN 12-18 | (0.005) | 0.012 | 0.014 | 0.004 | 0.014 | (0.006) (0.029) | $\begin{pmatrix} 0.002\\ 0.011 \end{pmatrix}$ | -0.001 | (0.007) | 0.022 | 0.014 0.096 | 0.004 | 0.008 0.048 | 990°0 600°0 |
| * 8 | | -0.004 | 0,009 | -0.007 | | | 0,005 | -0,006 | | 000.40 | 0.010 | -0.003 | (0.002) | $\begin{pmatrix} 0.007\\ 0.024 \end{pmatrix}$ |
| | 0.001 | 0.018 0.086 | 0.007 | 0.011 | 0.003 | | 0.010 | -0.006 | 0.002 | 0.010 | 0.014 | 0.010 | $\begin{pmatrix} 0.007 \\ 0.042 \end{pmatrix}$ | $\begin{pmatrix} 0.006 \\ 0.043 \end{pmatrix}$ |
| . 61 | 0,013 | 0,004 | 0.027 | 0,002 | 0.017 | 0.004 | | -0.005 -0.021 | 0.011 | 0.022 | -0.003 -0.017 | 0.007 | (0.008) | $\begin{pmatrix} 0.011 \\ 0.044 \end{pmatrix}$ |
| HOUR PST - | 0.009 | 0.030 | 0.011 | 670.0 | 0.030 | 0.012 0.068 | 0.002 | 0.014 | 0.003 | 0.033 | 0.034 | 0.003 | 0.016 | 0.012 |
| 10 - HUL | 0.015 | 0,025 | 0.010 | 0.018 0.055 | 0.033 | 0.007 | 0.001 0.006 | 0.027 | 0.024 0.085 | 0.013 | 0.009 | -0.002 | 0.015 | 0.011 |
| ; ; | 0.002 | 0.001 | 0,007 | 0.004 | 0.012 | 0.003 | 0.006 | 0.010 | 0,019 | 0.033 | 0.027 | 0.002 | 0.010 | 0.011 |
| 1 1 2 | | 0.003 | 0.013 0.046 | +0.002 | 0.003 | 0.004 | 0.009 | 0.006 | 0.001 0.00e | 0.021 | 0.016 | 0.030 | 600°0 | 0.010 |
| 10k ES | /kux | /wax | ZHUX | XUN/ | ZNOX | ZNOX | / NO X | ZNOX | /NUX | XIIN/ | /NUX | ZNOX | X D W N | /NUX |
| CONCENTRATION DIFFERENCES | Z Z Z | N N N N | Z Z | N N N N | 8 N N N | X N N | N N N | z z z | M M M | N N B N | 7 N H | Z Z | 2 Z 2 Z | , v Mr N.N. |
| Ct DAY t | ø | n | ၁ | 0 | ಬ | ù. | 9 | I | - | 7) | 4 | J. | ME.AN | SIO OFV |

TABUDALIUN UF DIFFERENCES AND NURMABIZED DIFFERENCES BY SPECIES

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| | • | | 1 | TABULATION OF | OF DIFFERENCES Resnirable | ES AND NORMALIZED PARTICULATE | Lizeo offeri Mate Samr | OIFFERENCES BY SE Sampler | SPECIES | | |
|------------|------------------------------|--------|----------------|-----------------|------------------------------|-------------------------------|---------------------------|------------------------------|----------------|----------------|------------------|
| DAY | CONCENTRATION DIFFERENCES | SNCES | | 1 20 | 10 - H | HOUR PST • 12 | 14 | . 91 | * 88 | MEAN 12-18 | STD DEV 12-18 |
| æ | NH4 NH4 | XNOX 1 | 1,040 | 1,400 | 1.690 6.790 | 1.490 5.980 | 1,370 | 0,400 | 1,250 | 1.128 | 0.495 |
| 20 | NH4 NH4 | XON/ | 0.670 | 0.190 | -0.110 | -0.760 | +0.220 -0.866 | 0.460 | 0.670 | 0.037 | 0.653 |
| υ | NH4 NH4 | /NUX | 0.670 2.350 | 0.280 | 0.390 | 0.540 | -0.690 | 0,400 | 0.060 | 0.078 | 0.550 |
| ے | NH4 NH4 | ZNUX | 0,360 | 1.030 3.330 | 0.820 2.510 | 0.520 | 0.150 | 1.240 | 0,750 | 0.665 | 0,456 |
| u i | AHN 44 | ZNOX | 0.470 | 0.130 | 1,720 | 1.920 | 0.600 | 0,360 | 0.790 | 0.918 | 0.691 3.028 |
| i <u>s</u> | NH4 NH4 | ZNOX | 0.100 | -0.070 0.101 | 1,460 | 0.320 | 0.710 | 0.460 2.530 | 0.460 1.600 | 0.488 2.158 | 0.162 0.528 |
| უ | N H 4 | /NUX | 0.500 | 0.610 | 0.790 5.130 | 0.050 | -0.430 | 0,120 0,541 | 1.270 | 0.227 | 0.732 2.312 |
| I | NH 4 NH 4 | /NDX | 0.370 | 0.420 | 0.520 | 0.490 | 0.540 | -0.200 | 0,360 1,240 | 0.298 | 0.340 |
| - | NH4 ₩#4 | /NUX | 0.520 | 0.230 | 5,320 18,800 | 0.370 | 0.410 | 0.300 | 0.390 | 0.368 | 0.048 |
| ר | AHN AHA | /NUX | 0.220 | 0.700 | 0,940 4,350 | 0.720 | 1.060 | 0.160 | 0,240 i,120 | 0.545 2.551 | 0.423 |
| × | NH4 NH4 | ZNOX | 0.370 | 0,660 | 0.820 | 0.370 | 0.570 | 0.330 3.080 | -0.010 | 0.315 2.189 | 0.241 |
| - 1 | NH4 NH4 | ZNCX | 0.100 | -0.100 0.388 | 0.650 8.550 | 0.800.7 | 0.690 4.060 | 1.090 8.650 | 1.670 | 1.087 | 0.421 |
| ME.AN | NH4 NH4 | /NUX | 0.449 | 0.457 4.726 | 1,251 | 0.569 1.475 | 0.397 | 0.427 | 0.658 | 0.513 2.138 | 0.123 0.341 |
| STO DEY | EV NHĢ. | /NUX | 0.265 9.819 | 0.446 15.236 | 1,388 4,679 | 0.681 | 0.601 2.541 | 0.392 2.586 | 0.518 1.902 | 0.548 3.144 | 0.123 1.633 |

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|---|----------------------|---------------|--------|----------------|------------------------|----------------|------------------|---|------------------------|---------------------------|
| - 450.0- XUUX | 0.034 | • | | 0.036 | 90.0 | 0.012 | 0.034 | 0.020 | 0.021 | 0.010 |
| NI -0.003 -0.005 NI /NOX 0.035 0.024 | 0.030 | • | | -0.003 | 0.005 | 0.002 | 000*0 | 0,005 0,016 | 0.003 | 0.002 |
| NI /NUX 0.019 0.008 | 0.011 0.039 0 | 99 | | 0.010 | 800°0 | 0.004 | 0.006 0.029 | 0.010 | 0.007 | 800°0 800°0 |
| NI 0.005 0.016 NI /NUX 0.015 0.052 | 0,005 0,015 0 | 0.016 | | 0,013 | 0.014 0.045 | 0.010 | 0,007 | 0.017 | 0.012 | 0.004 |
| NI /NUX -0.016 -0.032 NI /NUX -0.016 | 0.002 | • | | 0.020 | 0.024 | 0,009 | 0.008 | 600°0 | 0.011 | 0.009 |
| 160.0 - 600.0 - XUNX IN | 0,006 | • | | 0.007 | 0.013 | 0.009 | 0.004 | 0.004 | 0.008 | 0.004 |
| M1 /MOX -0.005 0.000 | 0.001 | | | -0.002 | 0,003 0,013 | 0.001 | 0.002 | 000.0 | 0.002 | 0.001 |
| NI /NUX 6,18U -0,038 | -0.058 0 6.18U -0 | 00 | | 0.002 | 0.003 | 0.004 | -0.001 -0.006 | 0.005 | 0.003 | 0.003 |
| NI /NUX 0,055 0,400 | 0 \$50.0 0 600.0 | 0 5 | | 0.004 | 000.0 | 0,006 | 0.001 | 0.012 | 0.005 | 0.005 |
| NI /NUX -0.013 0.091 | 0,005 0 | ၁ ၁ | | -0.002 | 0.012 | 0.001 | 0.001 | 000.0 | 0.005 | 0.006 |
| NI -0.002 0,005 NI /WUX 0.005 0.333 | 0.002 0 | 30 | | -0.006 | 0.016 | -0.002 | 0.010 | 0,003 | 0.007 | 850°0 800°0 |
| NI /NUX 0.005 0.058 | . 000°0- | • | | 0.005 | 0.002 0.016 | 0.006 | 0.008 | 0.005 | 0,005 | 0,002 |
| M1 /NUX 0.525 0.083 | -0.003 0 0.525 0 | 55 | | 0.005 | 0.009 | 0.004 0.018 | 0.004 0.028 | 0,006 0,021 | 0.006 | 0.002 |
| S10 DEV AL 0.008 NI /NUX 1.781 0.140 | 0,021 0 1,781 0 | 00 | | 0.008 0.039 | 0.007 0.038 | 0,004 0,015 | 0.004 | 0.005 | 0.005 | 0,002 |

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| Y X | CONCENTRATION DIFFERENCES | AT 10N NCES | | i i i 20 | HOU | HOUR PSF - | 1 14 | 1 91 | * 81 | MEAN 12-18 | STD DEV 12-18 |
|--------------|------------------------------|---|-----------------|-----------------|-----------------|------------------|------------------|------------------|----------------|---------------|------------------|
| ٩ | ON | X09/ | -0.256 0.862 | 0.834 0.834 | 0,201 | 0.153 | 0.163 | 0.129 | 0,205 0,798 | 0.163 | 0.032 0.085 |
| £ | N.C. N.C. | /NUX | -0.075 | -0.189 | -0.099 0.736 | 0.047 | 0,203 | 0.140 | 0.243 | 0.158 | 0.085 |
| ၁ | NO NO | / | 0,245 0,850 | 0.264 0.868 | 0.195 | 0.172 | 0.199 | 0.153 0.750 | 0.234 0.745 | 0.190 | 0.035 |
| ٥ | N N N | XOH/ | 0,185 0,554 | 0.108 0.350 | 0.115 0.352 | 0000.0 | 0.209 | 0.125 0.625 | 0.240 | 0.191 | 0.060 |
| 5 3) | 0 D Z | /HUX | -0.124 | -0.223 | 0.128 | 0.137 0.593 | 0.156 | 0.138 | 0.276 | 0.177 | 0.067 |
| <u>.</u> | ON | /NOX | -0.166 0.912 | -0.080 0.811 | 0.169 | 0.124 | 0,193 | 0.143 | 0.242 | 0.176 | 0.053 |
| ون | ON | XON/ | 0.932 | -0,084 1,010 | 0.123 0.799 | 0.160 | 0.197 0.738 | 0.163 | 0.265 | 0.196 | 0.049 0.049 |
| x | NO NÜ | NUX | -0.034 3.060 | 1.090 | 0.155 | 0.110 | 0.141 0.597 | 0.116 | 0.219 | 0.147 | 0.050 |
| - | ON | XON/ | 0.171 | 0.015 | 0.216 | 0.193 | 0.177 | 0.121 0.695 | 0.286 0.841 | 0.194 | 0.069 |
| ~ | N O | ZNOX | -0,393 1,020 | 0.054 0.818 | 0.189 0.875 | 0.105 0.495 | 0.092 0.429 | 0.070 | 0.165 0.771 | 0.108 | 0.041 |
| ¥ | 80 0 N | /NOX | 1,080 | 800°0 | 0.072 | -0.003 -0.020 | -0.007 -0.040 | ~0.069 -0.641 | 0.175 | 0.024 | 0.105 |
| د | N C | /H0X | 0.440 | -0.190 | 0.072 | 0.075 0.589 | 0.097 0.571 | 0.078 | 0.201 | 0.114 | 0.063 |
| S.A.N | ON NO | /NUX | -0,123 1,091 | -0.042 | 0.128 | 0.116 | 0.152 0.605 | 0.109 0.564 | 0.230 | 0.152 | 0.055 0.104 |
| ro dev | EV NO | ZNOX | 0.234 | 0.140 | 0.086 0.176 | 0.058 | 0.064 | 0.062 | 0.037 | 0.055 | 0.012 |

TABULATION OF DIFFERENCES AND NURMALIZED DIFFERENCES BY SPECIES

| | | | /1 | IABULATIUM UF | | S AMD MUKMAI Te Particu | DIFFERENCES AND NURMALIZED DIFFERENCES Respirable Particulate Sampler | ЪХ | SPECIES | | |
|----------|------------------------------|----------------|------------------|-----------------|----------------|----------------------------|--|----------------|------------------|----------------|------------------|
| DAY | CONCENTRATION DIFFERENCES | 41 [UN 4CES | 1 9 | , , , | 10 HG | наик PSI - | 1 4 1 | 1 9 1 | * 8 | MEAN 12-18 | STD DEV 12-18 |
| Ф | K 0 M | X047 | 0.730 | -0.150 | 0.100 | -0.360 | 000.0 | 0.480 | -0.010 | 0.027 0.318 | 0.345 1.702 |
| ລ | NU 3 NU 3 | ZNOX | 0,310 | 0.340 -1.630 | 0.520 | -0.190 | -0.320 | 0.050 | 0.020 0.064 | -0.110 | 0.176 |
| ၁ | 8.Ú.N 8.Ú.S | ZHUX | -0.160 | 0.220 | 0.280 1.150 | 0.490 | 0.110 | 0.150 | -0.010 | 0.185 | 0.214 0.883 |
| ے | NU3 NO3 | /NUX | -0,280 -0,838 | 0.070 | -0.190 | 0.420 | -0.220 | 0.380 | 0,053 | 0.158 | 0.301 |
| æ) | 809 803 | XUN1 | 0.160 | 0.380 | 1,100 | 0.320 | 0.230 0.916 | 0.690 | 0.341 1.050 | 0,395 | 0.202 |
| .3. | NO 3 NO 3 | /NUX | 0,560 4,408U | 0.300 | 0,530 2,830 | 0,310 | 0.390 | 0.400 | 0.040 0.139 | 0.285 1.392 | 0.168 0.888 |
| y | NU3 NU3 | NON | 0,580 | 0.760 | 1,290 | 0.110 | 0.260 | 0.840 3.780 | 0.170 | 0,345 1,434 | 0.336 1.581 |
| I | KU3 KO3 | /NUX | 0.270 | 000.0 | 0.990 4.650 | 0.600 | -0.570 | 0.050 0.298 | 0.200 | 0.070 | 0.486 2.073 |
| ¬ | NU3 NU3 | X0.4/ | 0,530 3,250 | 0.340 | 0.680 | 0.150 | 0,390 | 0.170 | -0.010 -0:029 | 0.175 | 0.164 0.695 |
| ״ | NU3 NO3 | ZNUZ | 0,320 | 0,230 3,480 | 0.770 | 0.990 4.670 | 1,580 7,350 | 0.610 | -0.440 | 0.685 3.210 | 0.850 3.905 |
| ~ | NO3 | ZNUX | 1,270 | 0.055 3.070 | 0.047 0.288 | 1,460 9,800 | 0,280 1,590 | 1.690 | 0.870 3.820 | 1,075 | 0,633 6,387 |
| د | RU3 RU3 | XUNIX | 0,770 -1,510 | 7.120 | -6.820 | 2.000 | 1,730 | 0.910 | 0,160 | 1.200 | 0.834 6.287 |
| MEAN | NO.3 NO.3 | X LIN X | 0.422 | 0.879 0.040 | -0.059 | 0.525 | 0,322 | 0.535 3.550 | 0.115 | 0.374 | 0.199 1.398 |
| SID DEV | NEV NU3 | /kux | 0.420 6.47b | 2,083 | 2.175 | 0.673 5.152 | 0,690 3,588 | 0.467 | 0,303 | 0.533 3.595 | 0.184 |

| CONCENTRATION DIREGENCES U3 / DOX | 2 | , b . 0 . 0 35 x 0 . 120 | | 10 10 -0,021 -0,085 | HOUR PSI 12 | 1 14 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 | 16 16 1 16 1 1 1 1 1 1 1 1 1 1 1 1 1 1 | 18 -0.032 -0.125 | MEAN 12-18 -0.036 | STD DEV 12-18 0.011 |
|---|-------------------|--------------------------|-----------------|------------------------------|---|--|--|------------------------|-------------------------|---------------------------|
| 0,009 0 0,009 0 0.009 0 0.009 0 0.009 0 0.009 0.009 0.009 0.009 0.009 0.009 0.009 0.009 0.009 0.009 0.009 0.009 | 0,009 | ээ 1 | 0.014 -0.068 | 0.032 | 0.013 | -0.034 -0.135 | -0.029 | -0.042 | -0.023 -0.045 | 0.024 |
| U3 /LUA -0.029 -0 | -0,029 |) i | 860°0- | -0.037 | -0.040 | -0.036 -0.133 | -0.025 -0.125 | -0.036 | -0.034 | 0.006 |
| 03 -0.615 -0.03 140X -0.040 -0. | -0.015 | 2 2 | -0.015 | -0.040 -0.124 | -0.040 | -0.041 | -0.629 | -0.042 | -0.039 | 0.007 |
| 03 0,003 0, 03 /kuX -0,021 -0, | 120.0- | ခံ ခုံ | 0.013 | -0.015 | -0.274 | -0.048 | -0.020 | -0.022 | -0.038 | 0.021 |
| 0.000 | 700°0- 000°0 | 0 | 0.008 | -0.008 | -0.021 | -0.041 | -0.019 | -0.015 | -0.024 | 0.011 |
| 03 0.011 03 780X -0.038 -0.131 | 0,008 -0,038 | 0.0 |)11 131 | -0.012 | -0.042 | -0.034 | -0.027 | -0.032 | -0.034 | 0.006 |
| U3 0,004 0,013 (13 /NUX -0,397 -0,161 | 0,004 - 792,0- | 0.0 | 61 | -0.027 | -0.070 | -0.080 -0.341 | -0.030 | -0.031 | -0.053 | 0.026 |
| U3 /HUX -0,003 0,005 U3 /HUX -0,013 0,530 | -0.002 | 0.0 | 30 | -0.041 | -0.048 | -0.037 | -0.021 -0.122 | -0.028 | -0.033 | 0.011 |
| 0.000 0.000 0.000 0.000 0.000 | 0.000.0 | 5.5 | 90 | +0.018 -0.084 | 650.0- 652.0- | -0.067 | -0,634 | -0,031 -0,143 | -0.047 | 0.017 |
| .0.017 -0.015 0.015 -0.015 0.016 -0.015 | -u.u1/ u.u4b | 0.0 | 15 36 | -0.00b -0.034 | 0.005 | *0.009 | 0.030 | 0.004 0.020 | 0.007 | 0.016 0.146 |
| 0103 - 0.010 - 0.010 03 //'UA 0.020 0.038 | 070 | 0.01 | ၁ 20 | 0,908 0,103 | 0.012 0.095 | 0.006 | 0.013 | 0,005 | 0.009 | 0.004 |
| 03 /MUX -0.065 -0.104 | -0.001 -0.005 | 0.0 | - | -0.016 -0.090 | -0.033 | -0.039 | -0.018 | -0.025 | -0.029 | 0.036 0.036 |
| 03 0.015 0.015 0.015 0.015 | 0,010 0,110 | 0.01 0.34 | V 4 | 0.021 | 0.029 | 0,023 | 0.019 | 0.016 | 0.022 | 0.005 |

TABULATION OF DIFFEFENCES AND MORMALIZED DIFFERENCES BY SPECIES

SC592.5FR Rockwell International

Atomics International Division Air Monitoring Center

| DAY | CONCEN | CONCENTRATION DIFFERENCES | : : : : | ; ; ; <u> </u> | • 0 | ноок PST - | , , | 1 0 | * 8 | MEAN 12-18 | STD DEV 12-18 |
|----------|---------------|------------------------------|------------------|----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|------------------|
| ٨ | ລະລະ | P8 P8 //PUX | -4,390 14,800 | -0.900 7.830 | 7.480 | 7.690 30.400 | 7.210 28.600 | 3.870 22.200 | 7.220 28.100 | 6.497 | 1.766 3.706 |
| a | 2.2. | РВ РВ 760X | -1.350 16.300 | -4.330 | -2.760 | 2.610 47.500 | 6.710 | 4,380 | 8.510 27.000 | 5.553 30.500 | 2,590 11,639 |
| ၁ | cu cu | PB PB /hUX | 8,880 31,200 | 9.460 31.100 | 8,410 | 7.510 | 5,240 19,400 | 4,590 22,500 | 7,350 | 6.173 24.075 | 1.478 |
| 2 | <u>⊸</u> ⊸. | PB ZNUX | 9,310 27,900 | 9.040 | 9.630 | 8.900 | 7,220 | 4,270 | 8.650 26.400 | 7.260 | 2.126 |
| ند | a, a, | PB PB /NOX | -1,430 | -3.160 | 7.010 38.700 | 8.770 38.000 | 7,270 | 4.250 | 8,200 25,200 | 7,123 | 2.012 |
| <u>u</u> | a. a. | PB ZNOX | -4,090 22,500 | 10.900 | 6,770 36,200 | 7,650 | 6.820 25.700 | 4.270 | 7,320 | 6,515 29,550 | 1,535 9,353 |
| IJ | 3. 3. | PIB PIB /NUX | -3,300 16,100 | -0.510 b.140 | 4.620 | 7.410 31.500 | 6,460 24,200 | 4,850 | 8.740 26.400 | 6.865 25.975 | 1.637 |
| x | - O- | PB / NOX | -2,320 | *0.440 5.500 | 6,480 30,400 | 6,810 | 7,090 30,000 | 4,310 25,700 | 7.530 | 6,435 27,825 | 1,447 |
| - | 3. G . | РН РВ //NOX | 5.870 36.000 | 1,040 | 8,610 30,400 | 7.210 | 6.820 28.300 | 4.860 27.900 | 9.020 | 6,978 27,425 | 1.706 |
| 2 | 34 3 <u>7</u> | РВ РВ //NGX | -7.610 19.800 | 4.050 61.400 | 7.190 | 7.800 36.800 | 7.890 | 5,490 25,900 | 000.0 | 7.060 | 1,360 6,264 |
| × | 3. J. | Рв Рв / лох | -7.480 | 2,150 143,000 | 7,500 | 7.320 | 6,810 38,700 | 4,390 41,000 | 6.420 28.200 | 6,235 39,250 | 1,284 8,612 |
| <u>-</u> | 3. 3. | РВ РВ /иОХ | -8.780 17.200 | -3.800 15.000 | 3,830 | 6.580 51.800 | 6.930 40.800 | 4.160 | 6.640 25,300 | 6.077 | 1,287 |
| MEAR | | PB //NUX | -1.391 | 0,955 37,314 | 6,281 | 7.188 | 6,872 | 4.474 | 7,782 | 6,579 | 1.453 |
| STD DEV | | PB / 180X | 6,208 55,253 | 4.557 | 3,271 | 1.593 8.761 | 0.629 | 0.424 | 0.886 | 0,883 | 0,510 |

TABULATION OF DIFFERENCES AND NURMALIZED DIFFERENCES BY SPECIES

| Αĭ | CONCENTRALIUN DIFFERENCES | CES | , , , , | 1 1 2 | 10 - hü | ъйи PSI - | 1 4 | , , , | * 8 | ИЕАN 12-18 | STD DEV 12-18 |
|--------|------------------------------|---------|-------------------|----------------|------------------|-----------------|----------------|------------------|----------------|------------------|------------------|
| ∢ | s s | /NUX | 2.66U -8.96U | 0.760 | -1,790 | -0.220 | -0.190 | -0.090 | -0.920 | -0.355 | 0.381 |
| £ | യ യ | /NUX | 0.200 | 2.120 | 665.0- | -0.130 | -0.630 | -0.600 | 10.890 | -0.562 -2.638 | 0.316 |
| | αw | ZNOX | 1.030 | -0.220 | 1.230 | 2,100 | -0.200 | 0.760 | 0.620 | 0.820 3.410 | 0.953 3.966 |
| _ | w w | /NUX | 1,200 3,590 | 2.190 | 1.800 | 3,350 | 0.760 | 3.230 16.100 | 2,220 6,770 | 2,375 | 1,226 |
| 1-2 | જ જ | ZNOX | 18,000 | 2,870 | 2,100 | 2.400 10.400 | 1,680 | 1.160 | 0.170 | 1.352 6.005 | 0.938 4.083 |
| | တ လ | ZNUX | 0.830 | 0.130 | -0.900 | 0,200 | -0.240 | -1.840 | -0.300 | -0.545 | 0.892 5.015 |
| | သ သ | /NOX | -0.520 2.540 | 0.120 | 0.240 | -0.360 | -0.630 | -0.500 | -0,660 | -0.538 -2.033 | 0.137 |
| _ | သ သ | /B0X | -5.520 502.000 | 0.700 | -0.240 | -1.100 | 1.210 | -0.100 -0.595 | 0.540 | 0.138 | 0.983 4.176 |
| | တ သ | XNN/ | -0.670 -4.110 | 126,000 | -0.500 | 1.200 | 0.250 1.080 | 0.450 2.590 | 1,910 5,620 | 0.955 3.445 | 0.755 |
| | တ တ | X D N Z | 0.020 | -0.760 | -0.740 -3.430 | -0.460 | -0.580 | -0,350 -1.650 | 000.0 | -0.463 | 0.115 0.525 |
| | သ သ | /NOX | 0,360 | -0.100 | -0.450 | -0.430 | 000.0 | 0.050 | 0,140 | -0.060 | 0.253 1.646 |
| | o o | /NUX | 086*0- | 0.140 | -0.190 | 0.490 3.860 | -0.200 | -0.640 -5.080 | -0.650 | -0.250 | 0.536 3.755 |
| Z A | യ യ | /NUX | 0.193 39.307 | 0.554 7.171 | 0.053 0.039 | 0.567 | 0.098 0.342 | 0.128 | 0.198 | 0,25,3 0,854 | 0.227 |
| 430 d | S S | 7h0x | 2.054 145.835 | 1.082 | 1.140 | 1.375 | 0.741 2.994 | 1.240 | 1.070 | 1.106 | 0.274 |

TABULATION OF OIPPERENCES AND NURMALIZED DIFFERENCES BY SPECIES

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| | STU UEV 12-18 | 0.008 | 0,015 | 0,008 | 0.001 | 0.002 | 0.004 | 0.007 0.039 |
|---|---------------------------------------|------------|----------------|----------------|----------------|----------------|----------------|----------------|
| | MEAN 12-18 | 0.010 | -0.009 | 0.020 | 0.012 | 0.004 | 6.007 0.040 | 0.012 |
| SPECIES | * » | 0.002 | -0.027 | 0.032 | 0,013 0,055 | 0.001 | 0.004 | 0.021 |
| RENCES BY S | | 0.005 | -0.017 | 0.018 0.084 | 0.012 | 0.002 | 0.004 | 0.013 |
| JIZED DIFFE | · · · · · · · · · · · · · · · · · · · | 0.017 | 0.002 | 0.016 | 0.010 | 0.005 | 0.010 | 0.007 |
| TAGULATION OF DIFFERENCES AND NORMALIZED DIFFERENCES BY | HOUK PSf - | 0.015 | 0.005 0.018 | 0.015 | 0.012 | 0.006 0.044 | 0.010 | 0.005 |
| DIFFERENCE | 1 0 | 0.015 | 0.011 | 0.011 | 0.010 | 0,006 | 0.011 | 0.003 |
| SULATION UP |) 1 1 | 0.003 | 0.8.0 900.0 | | 0,007 | 0.014 | 0.008 | 0.004 |
| I.A | : : : : : | 0.012 | 0.010 | | 0.001 | 0,002 | 0.000 | 0,000 0,545 |
| | 5.5 5.3 5.3 | ZNUX | / NUX | /hux | 7 N D X | 750.8 | ZNUX | / IN 11 X |
| | CUNCERTRATION DIFFERENCES | 802 802 | \$0\$ \$0\$ | \$42 \$02 | \$0.2 \$0.2 | 802 802 | \$0.2 \$0.2 | EV 502 SU2 |
| | DAY | Ŧ | _ | ت | ጙ | ٦ | MEAU | STD DEV |

Air Monitoring Center

| | | | # 1 | TABULATION OF | | DIFFERENCES AND NURMALIZED DIFFERENCES BY Resnirable Particulate Samnler | uzeo oreren Ulate Sam | | SPECIES | | |
|-----------|------------------------------|------|-----------------|-----------------|-----------------|---|--------------------------|-----------------|----------------|----------------|------------------|
| UAY | CUNCENTRATION DIFFERENCES | JON | ! | | | HOUR PST 12 | 1 4 | 1 9 1 | * 80 | MEAN 12-18 | STD DEV 12-18 |
| ∢ | SU4 SU4 | ZNOX | 1,200 | 2,300 | 2,900 | 2,500 | 2,200 8,730 | 2.630 | 0,220 0,856 | 1.688 | 1,126 |
| Ð | SU4 SU4 | /NUX | 0.740 | 0.930 | 1.400 | 1,440 | 0.550 | 0.380 | 0.760 | 0.783 8.153 | 0.465 12.034 |
| O | 504 504 | ZNUX | 0,300 | 0,500 | 1.700 | 1.600 | 0.100 | 1.160 | 1,370 | 1.058 4.258 | 0.663 |
| ے | \$U4 \$U4 | /NUX | 2,200 | 2.500 8.090 | 3,400 10,400 | 2.400 | 1,600 | 2,400 | 0.200 | 1.650 | 1.038 |
| iai. | \$U4 \$D4 | ZUNZ | 2,100 | 1.400 | 4,300 23,800 | 5,200 | 1,400 5,580 | 0.890 4.920 | 1,670 | 2.290 9.530 | 1,967 8,651 |
| <u>u.</u> | \$U4 \$04 | /NOX | 0.580 | 0.930 | 1,800 9,630 | 1,530 8,690 | 1,840 | 0.480 | 0.870 | 1,180 | 0.618 2.967 |
| 9 | SU4 SU4 | XON/ | 0.790 | 1,500 | 2,900 18,800 | 2,900 | 0.410 | 1,520 6,850 | 1,780 | 1,355 5,618 | 1.139 |
| Z | \$04 \$04 | ZUNZ | 0,600 | 0.700 | 2,900 | 2,700 11,700 | 0.500 | 2,060 12,300 | 0.900 3.100 | 1.540 | 1.018 |
| - | 504 504 | ZNOX | 2,000 12,300 | 000.06 | 1.800 6.360 | 1.800 | 0.800 | 1.260 | 0.720 | 1,145 4,855 | 0.497 |
| ר | SU4 S04 | /NUX | 066*0- 088*0 | 0.470 | 0.800 3.700 | 0.460 | 1.180 | 0.440 | -0.390 | 0.422 | 0.642 2.989 |
| × | SU4 SU4 | /NUX | 900°0 | -0.160 | 1,090 | 0.580 3.890 | 000.0 | 0.030 | 0.740 | 0,338 | 0.378 |
| ı, | SU4 S04 | /NUX | -0.740 1.450 | -0.100 0.388 | 0.190 | 0.490 3.860 | 0.600 | 1.370 | 3.000 | 1.365 | 1.158 |
| МЕ.А И | \$04 \$04 | ZNUX | 0.846 -5.418 | 0.989 | 2.098 8.640 | 1.967 | 0.932 3.759 | 1.218 6.819 | 0,888 3,026 | 1,251 | 0.499 |
| sry vev | 5V SO4 SU4 | /NUX | 0.892 16.938 | 0.828 28.923 | 1.192 8.564 | 1.326 | 0.704. | 0.831 4.812 | 0.853 3.231 | 0.929 | 0.273 |

| | STU DEV 12-18 | 0.679 2.648 | 0.751 | 0.622 | 1.117 | 3,281 | 0.814 4.286 | 0.532 | 3,350 | 1.181 | 0.564 | 1.658 9,300 | 1.725 15.046 | 0.237 | 0.470 |
|--|---|------------------|------------------|----------------|-----------------|-----------------|-----------------|-------------------|---------------------|--------------|------------------|-------------------|-------------------|------------------|-----------------------|
| | MEAN 12-18 | -0.955 -4.132 | -2.007 | 1.700 | 4,700 | 2.588 11.630 | -2.057 | -2.938 -11.470 | -0.682 -3.483 | -0.823 | -1.747 -8.197 | -2.320 -14.905 | -2,733 | -0.567 | 2.812 12.750 |
| SPECIES | * 8 * * * * * * * * * * * * * * * * * * | -1.710 | -2,800 | 2.000 | 5,200 | -1.420 | -1.620 | -2,970 -8,970 | 1,370 | 000.0 | 0.00.0 | -0.780 -3.420 | -0.600 | -0.333 -1.323 | 2,517 7,95b |
| DIFFERENCES BY SE | , o | -0.810 -4.660 | -2.600 | 1.400 5.860 | 4.100 | 1,770 | -1.140 | -2.880 -13.000 | -0.400 | -1.770 | -1,300 | -1.500 | -4.800 -38.100 | -0.778 | 2,319 |
| NUKMADIZED DIFFE | 1 4 | -0.100 | *2.230 *8.780 | 1.000 | 3,500 11,600 | 6,400 | -2,870 | -2,300 -8,610 | 1,800 | -1.200 | -1.560 | -4.600 -25.100 | -2,540 | -0.392 | 3.098 |
| | иоок PST 12 | -1,200 | -1.000 | 2,400 9,920 | 6.000 19.400 | 3,500 15,600 | -2,600 | -3,600 | -5,500 | 0.500 | -2.380 | -2,400 | -2,990 | -0.764 | 3,313 |
| DIFFERENCES AND 1 Particulate | . 0. | -4,000 | -1,100 8,150 | 1.700 | 5.700 | 3,300 18,200 | -3.100 | -3.700 | -1.5,900 | -4.000 | -2.520 | -3.190 | -2,126 | -1.386 | 3.215 16.163 |
| TABULALIUM OF DIFFERENCES AND TOTAL PARTÍCULATE | ; ; ; 20 | 4,800 | 0.900 | 0.700 | 4.600 | 4,700 | 040.4 | 000.0 | -2.000 | -4.00.000 | -1.320 | -1.060 | 0.870 | 0.632 | 2.809 115.472 |
| 41 | ; ; ; | 11,900 | 0.800 | 0.10U 0.351 | 3,100 9,280 | 5.200 | 0.030 •0.165 | 0.300 | -17.000 1550.000 | -3,800 | 2,110 | 2.330 | 2.520 | 0.632 118.860 | 6,701 450,974 |
| | 30 8 | ZNUZ | /NUX | / NUX | ZNUZ | ZNOX | / HOX | / kux | /#UX | /kux | ZUNZ | /NUX | /NUX | /NUX | ZEUX |
| | CONCENTRATION DIFFERENCES | SU4 SU4 | 504 504 | \$114 \$114 | \$04 \$04 | \$04 \$04 | SU4 SU4 | SU4 | SU4 SU4 | SU4 S04 | S04 S04 | S04 S04 | \$0.4 \$0.4 | \$0.4 \$0.4 | \$11 4 \$U4 |
| | DAY D | ব | £ | Ú | a | zì. | ı. | G | E | - | 2 | × | -J | ME.AW | STO UEV |

| | STD DEV 12-18 | | 0.062 | | | | | | | | | | 0.017 |
|---|------------------------------|----------------|----------------|----------------|-------|-------|--------|-------|----------|----------------|----------------|-------|-----------------------|
| | MEAN 12-18 | | 0.044 0.660 | | | | | | | | | | 0,013 0,083 |
| SPECIES | * 81 | | 0.018 0.057 | | | | | 0.019 | | | | | 0.003 |
| | 1 0 | | 0,006 | | | | | | 0.032 | | | 0,028 | 10.006 |
| JZED OIPFER | 1 4 1 | | 0,016 | 0.037 | | | -0.011 | | | | 0.162 | | 0.029 |
| S AND MURMAL | HOUR PST - | 0.098 0.394 | 0.137 | | | | 0.064 | | | | 0.180 | | 0.025 |
| DIFFERENCES | 10 - HOL | 0.095 | 0.061 | 0.060 0.247 | | 0.917 | | 0.071 | | 0.148 | 0.024 | 0.051 | 0.014 |
| TABULATIUM OF DIFFERENCES AND MURMALIZED DIFFERENCES BY | ; ; ; ∞ | 0.052 | 0.053 | 0.136 | 0.073 | 0,015 | 0.017 | | 0.083 | 0,051 5,100 | 0.138 2.090 | 0.267 | 0.063 |
| 1 A | ; ; ; | 0,014 | 0.066 | 0.081 | 0.037 | 0.033 | -0.007 | | 0.031 | | 0.027 | 0.112 | 0.162 |
| | 1014 S.S. | /NOX | /NOX | ZNNZ | ZNNZ | /PUX | X04/ | /NUX | ZUNZ | XUN/ | ZNOX | /NUX | /EUX |
| | CONCENTRALIUM DIFFERENCES | 11 | 11 11 | 11 11 | 11 | 11 | == | 11 | 11 11 | 11 | | 11 | und parti Gua (cm. |
| | DAr | 4 | Ð | o | ٦ | æ | بد | 9 | x | - | ٦ | × | ت |

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| STD DEV 12-18 | 0.014 0.041 | 0.010 | 0.009 | 0.021 | 0.031 0.135 | 0.022 | 0.012 0.057 | 0.025 0.086 | 0.011 | 0.013 | 0.020 | 0.015 | 0,014 0,083 | 0.005 |
|------------------------------|----------------|-----------------|----------------|----------------|----------------|-----------------|-----------------|---|----------------|----------------|----------------|-----------------|----------------|---------|
| NEAN 12-18 | 0.044 0.186 | 0.035 | 0.038 0.151 | 0.048 0.167 | 0.053 | 0.047 | 0.039 | 0.049 | 0.034 | 0.058 | 0.047 | 0.043 | 0.044 | 0.012 |
| * æ | 0,038 0,148 | 0.039 | 0.043 | 0.046 | 0,029 | 0.039 | 0.033 | 0,062 0,214 | 0.019 | 000.0 | 0.052 0.228 | 0.041 0.156 | 0,040 | 0.011 |
| , , 4 , 4 | 0.027 | U.021 0.101 | 0.029 | 0.027 0.135 | 0.029 | 0.021 | 0.025 0.113 | 0.024 | 0.032 | 0.043 | 0.027 | 0.022 | 0.027 | 0.006 |
| . 44 | 0.055 0.218 | 0.043 0.169 | 0.034 0.126 | 0.042 | 0.062 | 0.070 | 0.044 0.165 | 0.077 | 0.043 | 0,068 | 0,035 0,199 | 0.053 | 0.052 | 0.014 |
| HUUR PST 12 | 0.056 0.225 | 0.038 8£0.0 | 0.048 0.198 | 0.078 | 0.093 | 0.060 | 0,053 | 0.033 0.143 | 0.043 | 0.064 | 0.073 | 0.055 | 0.058 | 0.017 |
| . 0 | 0.059 | -0.021 0.156 | 0,060 | 0.062 | 0.077 | 0.067 | 0.021 | 0.068 0.319 | 0.062 0.219 | 0,045 0,208 | 0,052 | 0.053 | 0.050 | 0.027 |
| 1 1 1 1 ∞ | 0.007 | -0.030 0.144 | 0.085 | 0.066 | 0.005 | -0.005 0.051 | 0,001 | 0.003 | 0.010 | 0.069 1.050 | 0.057 | -0.045 | 0.019 0.548 | 0.041 |
| i i | 0.021 | -0.003 0.03 | 0.059 | 0.058 0.174 | 0.014 | -0,025 | -0.010 0.049 | -0.073 6.640 | 0.030 0.184 | -0.009 | -0.008 | -0.034 0.067 | 0.002 0.613 | 0.038 |
| TUNES | ZHOX | /PUX | ZNUX | ZNOX | /NOX | ZNDX | X IN O.X | X D N / | X D N / | XUNZ | XONZ | XNUX | /h0% | /NUX |
| CONCENTRATION DIFFERENCES | 22 kg | N 7. | N N 7 7 | 2 S 2 S | N 7. | 2 N Z | 2 N 2 N | 7 N 7 7 N 7 N 7 N 7 N 7 N 7 N 7 N 7 N 7 | 2 N 2 N 2 N | N 27 | N 2 7 7 | N7. | 2 Z Z | V 2 V |
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FABULATION OF DIFFERENCES AND NURMABIZED DIFFERENCES BY SPECIES

Rockwell International

| 7 | CUBCENTRATION DIFFERENCES | | • • • • • • • • • • • • • • • • • • • | Ont: | io , | al Dart | al Particle Coun | al Particle Counter 0.75 | Particle Counter O. | al Particle Counter (1.75 /m) - HOUR PSI 10 18 10 18 | , = |
|----------|------------------------------|--------------|---------------------------------------|--------------------|-------------------|-------------------|------------------|--------------------------|---------------------------------|---|-------------------|
| | | / INDX | 000.0 | 000.0 | 000.0 | 55 | 000.0 | 000°0 000 | | 0.000 0.000 | 000.0 000.0 000.0 |
| | | /ku% | 000*0 | 000.0 | 000.0 | 000°0 | | 000.0 | | 000.0 | 000*0 000*0 |
| o o | | Z047 | 000.0 | 000.0 | 000.0 | 000.0 | | 0.00.0 | 000*0 000*0 | | 000*0 |
| ے | | 7803 | 000.0 | 000*0 | 000.0 | 0.00.0 | | 000000 | 000.0 000.0 | | 000.0 |
| ليد | | ZNOX | 000.0 | 000.0 | 0.00.0 | 000.0 | | 000.0 | 000.0 000.0 | | 000*0 |
| | υ≈,75υ υ≠,/5υ | ZWUX | 67.160 -372.000 | 82,900 -837,000 | 93,500 | 62,400 355,000 | | 33,700 127,000 | 33,700 16,100 127,000 88,500 | | 16.100 88.500 |
| | D≥.750 D≤.759 | ZEGZ | 20.800 | 30,500 | 48.400 314.000 | 30,000 128,000 | | 13.000 | 13,000 15,500 48,700 69,800 | | 15.500 |
| | 0=.750 0=.750 | /40 <i>%</i> | 42,200 | 53,800 | 59.100 277.000 | 60,100 261,000 | - | 27.100 115.000 | 27,100 2,900 15,000 17,300 | - | 2,900 |
| | υ=, 75α υ=, 75υ | XUMX | 51,000 374,000 | 62,500 6290,000 | 64,900 229,000 | 38,200 143,000 | | 23,100 95,900 | 23.100 15.400 95.900 88.500 | - 2 | 15.400 88.500 |
| | υ≃./5υ υ≃./5υ | XORX | 0.00.0 | 429,000 | 21,100 | 29,300 138,000 | | 17.000 | 17.000 9.560 79.100 45.100 | | 9.560 45.100 |
| | υ≃./5υ υ≃./5υ | אויטא | 23.800 | 58,800 3920,000 | 49.400 303.006 | 25,400 170,006 | | 31,200 | 31,200 33,700 77,000 315,000 | ~1 | 33,700 315,000 |
| | υε. 750 υε. 750 | 7808 | 30.200 -59.200 | 40,860 -158,000 | 33.400 439.000 | 21,200 | - | 17,700 104,000 | 17,700 47,100 04,000 374,000 | | 47.100 |
| ik. A is | υ=.75υ υ=.75υ | 740% | 40.95u | 51,200 1226.5/1 | 52,429 304,529 | 38.086 194.5/1 | - | 23.257 106.671 | 23.257 20.037 | | 20.037 142.000 |
| TD OEV | v b=,750 v=,750 | ZEUÄ | 19.071 | 19,369 2764,788 | 23.291 | 16.050 #3.472 | | 7.769 | 7,769 15,166 40,151 141,202 | - | 15,166 |

| | STD DEV 12-18 | 000.0 | 000.0 | 0.00.0 | 000.0 | 0.00.0 | 1.940 | 0.153 | 0.919 | 0.177 | 0.160 | 0.652 | 1,669 | 0.218 2.938 | 0.762 |
|--|------------------------------|--------|--------|--------|-------|-----------------|------------------|------------------|----------------|-------------------|------------------|-----------------|------------------|------------------|----------------|
| | MEAN 12-18 | 000.0 | 000.0 | 000.0 | 000.0 | 000.0 | 1,280 | 0.740 | 0,610 2,195 | 0.735 2.895 | 0.733 3.435 | 2.050 14.208 | 3.168 18.738 | 1,331 | 1.193 |
| SPECIES | * 89 | 000.0 | 000.0 | 000.0 | 000.0 | 000.0 | -1.230 | 0,930 | 0.810 2.790 | 0.900 | 0.870 | 1,740 | 5,380 | 1,343 | 1,998 7,030 |
| В. Т | | 000.0 | 000.0 | 000.0 | 000.0 | 000.0 | 3.470 | 0.710 | -0.640 | 0.510 | 0,520 | 3.000 | 3,470 | 11.577 | 1.689 |
| мартиер отневкемсея Counter 1.33 µm | . 4. | 000.0 | 000.0 | 000.0 | 000.0 | 000.0 | 1.170 | 0.560 | 0.700 | U.680 2,820 | 0.700 | 1,920 | 1,590 9,350 | 1.046 | 0,530 3,519 |
| . AMU MURBAL | ntibis PSF - 12 | 000.0 | 000.0 | 000.0 | 000.0 | 000.0 | 1.710 | 0.760 3.230 | 1.5/0 | 0.45U 3.180 | 0.84U 3.960 | 1.540 | 2.230 | 1,357 | 0,555 |
| or otherweses and mundables of Ferences Optical Particle Counter 1.33 µm | 10 - BUD | 0,000 | 0.00.0 | 090°0 | 000.0 | 000.0 | 2.540 13.000 | 1.320 | 1,550 | 1.040 | 0.910 4.210 | 2.530 | 2.470 | 12,494 | 0.061 |
| тавита глем тив Ор | ; ; | 0,000 | 000.0 | 000.0 | 000.0 | 0.00.0 0.000 | 2.070 | 0.560 | 1.190 | 000 * +\$1 | 1,200 19,100 | 2,300 | 2.710 | 1.001 | 0.740 |
| 1.A.1 | ; ; | 0000.0 | 000.0 | 000.0 | 000.0 | 000.0 | 1.880 | 0.240 | 1,140 | 1.48u 9.080 | 0.000 | 0,47u -2.62u | 1.910 | 1.276 | 0.631 |
| | | 7603 | 7513.8 | 71401 | Znux | ZHOA | /EUX | 7,40,4 | Zbūž | Zeuk | 715(3.8 | 7413.K | 7 to 0 X | 7603 | / 1013 X |
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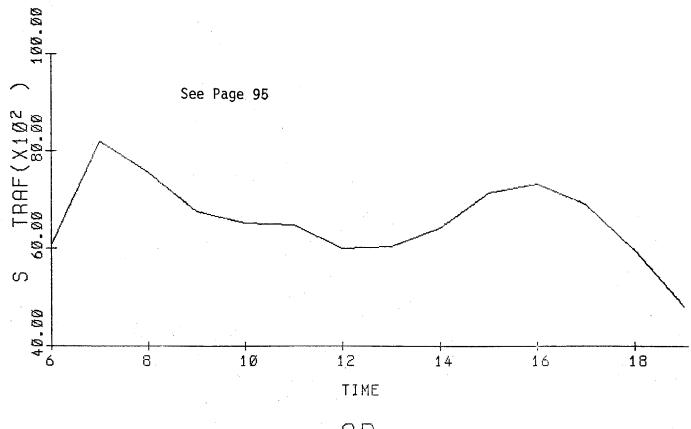
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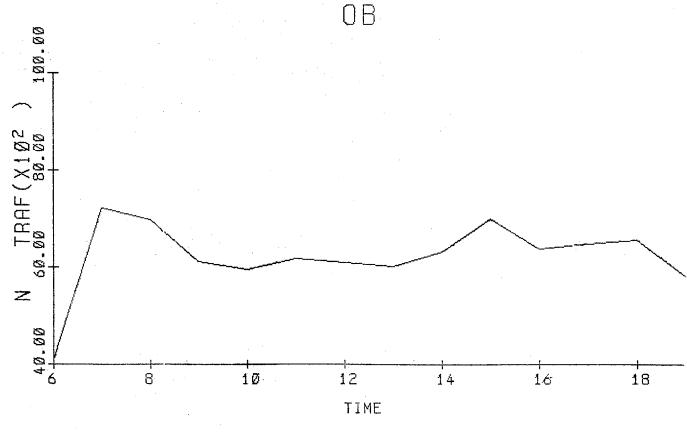
| | | | 3 | LARGEATTUR O | POTFERENCE Dotical P | OP DIFFERENCES AND WORMANIZED DIFFERENCES BY OPTICAL PARTICLE COUNTER 2.37 um | uizeo oikke Junter 2. | RENCES BY SF 37 um | SPECIES | | |
|--------------|-----------------------------|--------|-----------------|-------------------|----------------------|---|--------------------------|-----------------------|----------------|----------------|------------------|
| λψCi | CHACENTRATIUM DIMMEMENES | 2 g | · · · · · | , , , , | H | HOUR PST - | 1 1 4 1 | | , 18* | MEAN 12-18 | STP DEV 12-18 |
| વ | | 7408 | 090*0 | 000.0 | 000*0 | 0.00.0 | 000.0 | 000.0 | 000.0 | 000.0 | 000.0 |
| £ | | ZEUX | 0.00.0 | 000.0 | 000*0 000*0 | 000.0 | 000000 | 000.0 | 000.0 | 000.0 | 000.0 |
| S | | ZEUX | 000*0 | 000.0 | 000*0 | 0.00.0 | 000.0 | 000.0 | 000.0 | 000.0 | 000.0 |
| ټ | | ZNOX | 000.0 | 000.0 | 000*0 | 000.0 | 000.0 | 000.0 | 000.0 | 000.0 | 000.0 |
| .e. | | /HÜX | 0.00.0 | 000.0 | 000*0 | 000°0 | 000.0 | 000.0 | 0.00.0 | 000.0 | 000.0 |
| ı. | U=2.37 U=2.37 | ZiitiX | -0.005 | 0.028 | 0.073 0.190 | 0.015 | 0.036 | 0.107 | -0.021 | 0.034 | 0.054 |
| و. | U=2.31 U=2.31 | ZINAZ | 0.111 | 1.400 | -0.015 | -0.043 | -0.026 -0.097 | 0,028 0,126 | -0.001 | -0.011 | 0.031 0.132 |
| £ | 0=2,37 U=2,37 | /1,03 | 0.621 | -0.066 | -0.003 | -0.031 | -0.078 | -0.238 | 0.024 0.083 | -0.081 | 0.113 0.668 |
| | 0≈2,37 0≈2,37 | ZRUX | -0.031 | -0.122 -12.200 | -0.454 | -0.050 | 0.004 | -0.028 | -0.024 | -0.025 | 0.022 |
| ث | 78.5±0 78.5±0 | ZNUX | 0.00.0 | -0.160 | -0.251 | -0.203 -0.958 | 0.797 3.710 | -0.145 | -0.199 | 0.062 0.285 | 0.490 |
| ¥ | 0=2,37 0=2,37 | /hux | -6.135 0.305 | -0.076 | -0.019 | 900.0 | 0,057 | 0.213 | -0.013 | 0.066 | 0.102 |
| _ | 0=7.37 v=2.57 | ZhuX | 0.093 | U.146 | 0.120 | 0.102 | 0.085 | 0.010 | 0.067 | 0.066 0.410 | 0.040 |
| स्टिक् स | D=2.37 D=2.37 | ZPHA | 120.0- | -0.051 | -0.021 0.056 | -0.029 | 0.125 0.608 | -0.008 0.074 | -0.024 | 0.016 | 0.073 |
| JP ocy | rV 0=2,37 | 75:103 | / RO* 1 | 0.106 | 0.118 0.820 | 0.520 | 0.301 | 0.150 1.065 | 0.084 | 0.157 0.839 | 0.101 |

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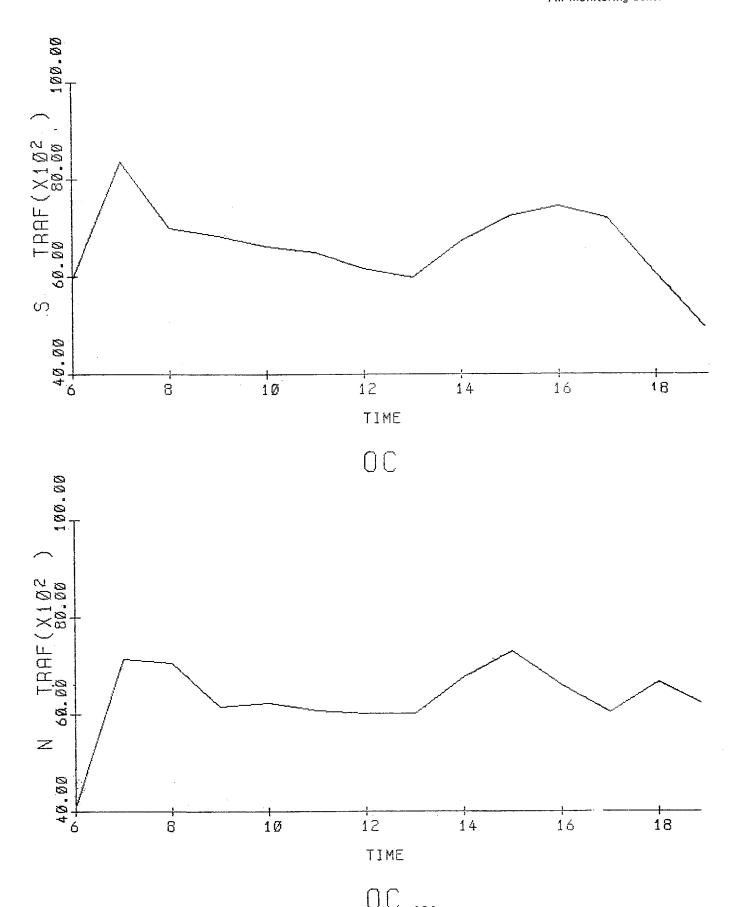
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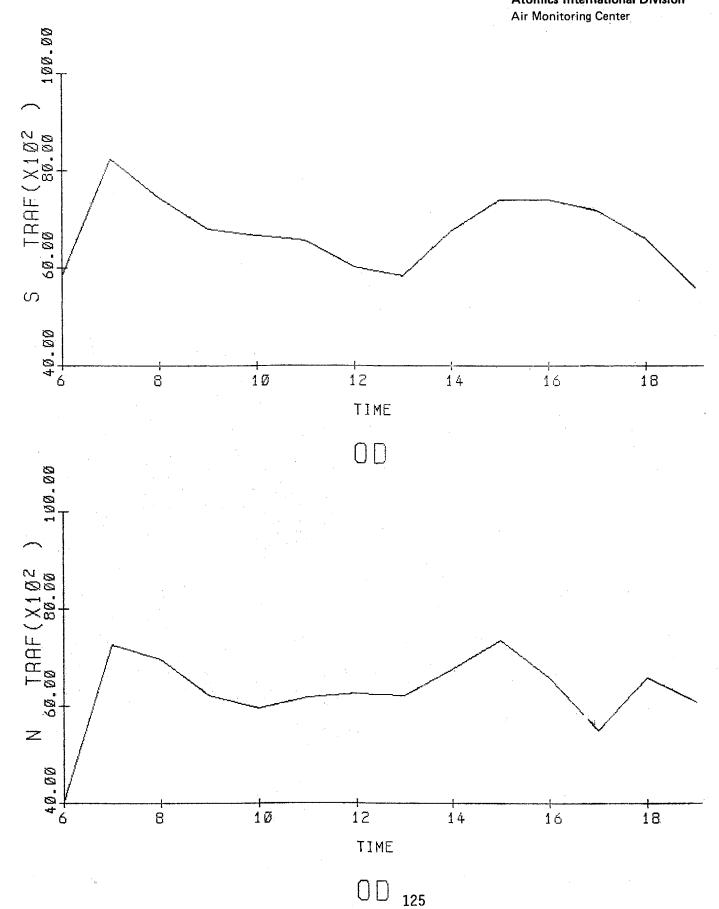
| | STD DEV 12-18 | 000.0 | 0.00.0 | 000*0 | 000.0 | 000.0 | 0,007 | 0.022 | 0.026 | 0.011 | 0.483 2.246 | 0.026 | 0.041 0.352 | 0.066 | 0.165 |
|--|------------------------------|--------|--------|--------|--------|--------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| | MEAN 12-18 | 0000.0 | 000.0 | 0000.0 | 000.0 | 000.0 | 0.040 | 0,052 0,195 | 0.023 | 0.046 0.184 | 0.274 | 0.085 | 0.057 | 0,082 0,416 | 0.114 |
| PECLES | * 81 | 000*0 | 000.0 | 000.0 | 0.000 | 000*0 | 0.034 | 0.082 0.248 | 0.048 | 0.060 | 0.015 | 0.064 | 0.026 0.098 | 0.047 0.166 | 0.024 |
| н¥ | 16 | 000.0 | 0000.0 | 000.0 | 0000.0 | 000.0 | 0.049 | 0.054 | -0.024 | 0.041 | 0.012 | 0.122 | 0.028 | 0.043 0.306 | 0.040 0.384 |
| rabutalium uf differences amu nurmalized differences hy species Optical Particle Counter 4.21 $\mu \mathrm{m}$ | 1 1 1 | 000.0 | 000.0 | 000*0 | 0000.0 | 000000 | 0.042 0.158 | 0.035 0.130 | 0.006 | 0.047 | 0,997 4,640 | 0.081 | 0.060 | 0.181 0.852 | 0.360 |
| | HOUR PST - | 000.0 | 0000.0 | 000.0 | 000.0 | 000.0 | 0.034 | 0.038 | 0.041 | 0.034 | 0.072 | 0.071 | 0.114 0.898 | 0.058 0.339 | 0.030 0.275 |
| | 1 01 · | 000.0 | 000.0 | 000.0 | 000000 | 000.0 | 0.097 0.519 | 0.100 | 0.385 0.385 | 1.020 3.600 | 0.020 | 0.092 | 1.090 | 0.213 0.986 | 0,357 1,191 |
| SUCABION OF OPPOSICA | 1 1 20 | 000.0 | 000.0 | 0000.0 | 000.0 | 000.0 | 0.072 | 0.040 | 0.055 -0.663 | 0.039 3.900 | 0.078 1,180 | 0.122 8.130 | U.146 •0.566 | 0.079 1.539 | 0.041 3.358 |
| IAE | 1 1 | 000.0 | 000.0 | 000*0 | 00000 | 000.0 | 0.038 | 0.035 | 0.00 ° 8 • 0.00 | 0.047 | 0.00°,0 | 6.060 -0.162 | 0.119 | 0.065 | 0,033 3,232 |
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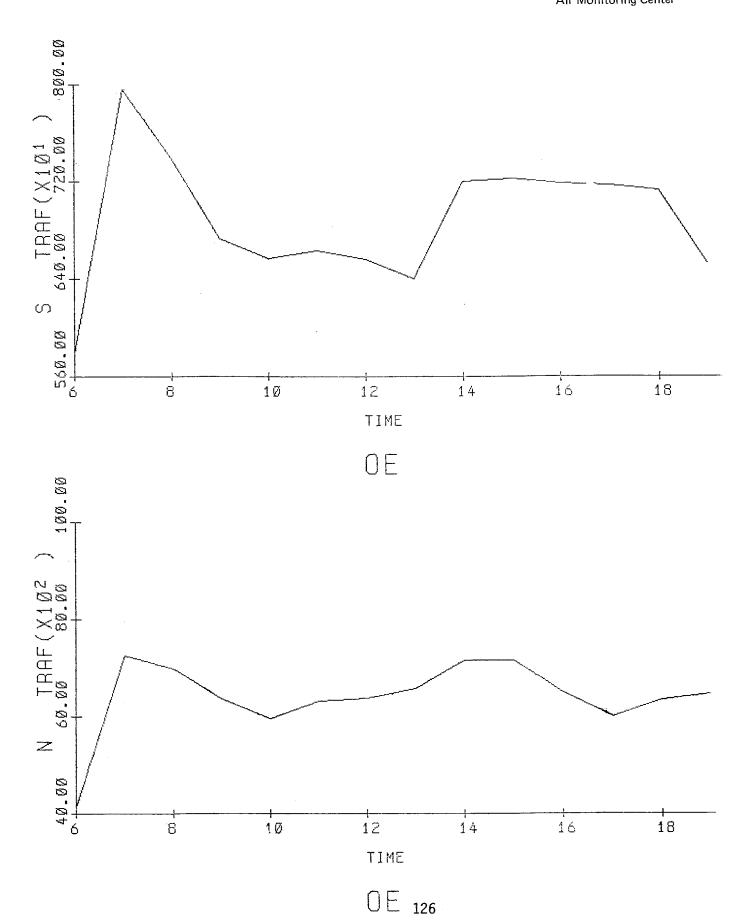


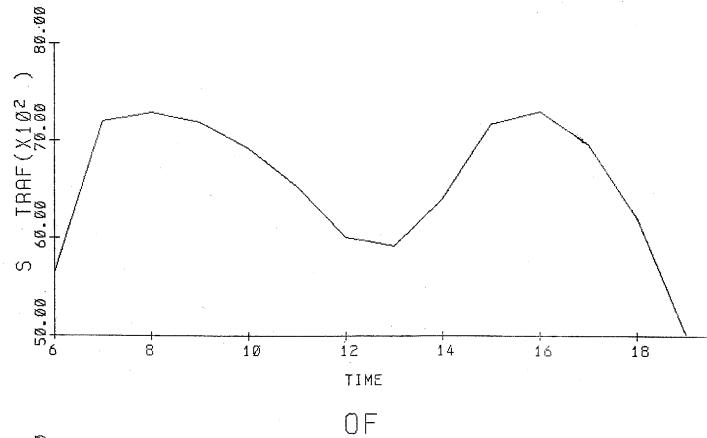


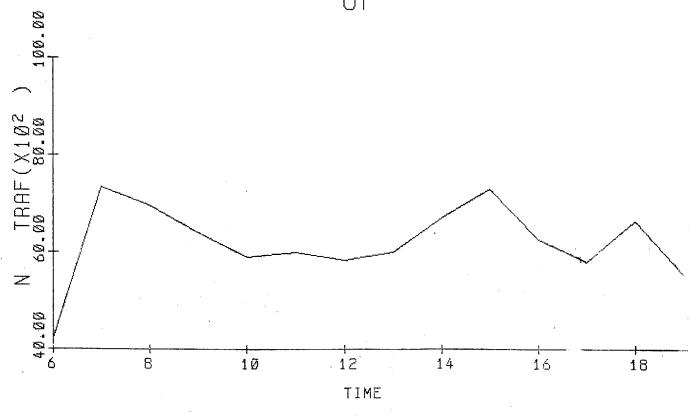
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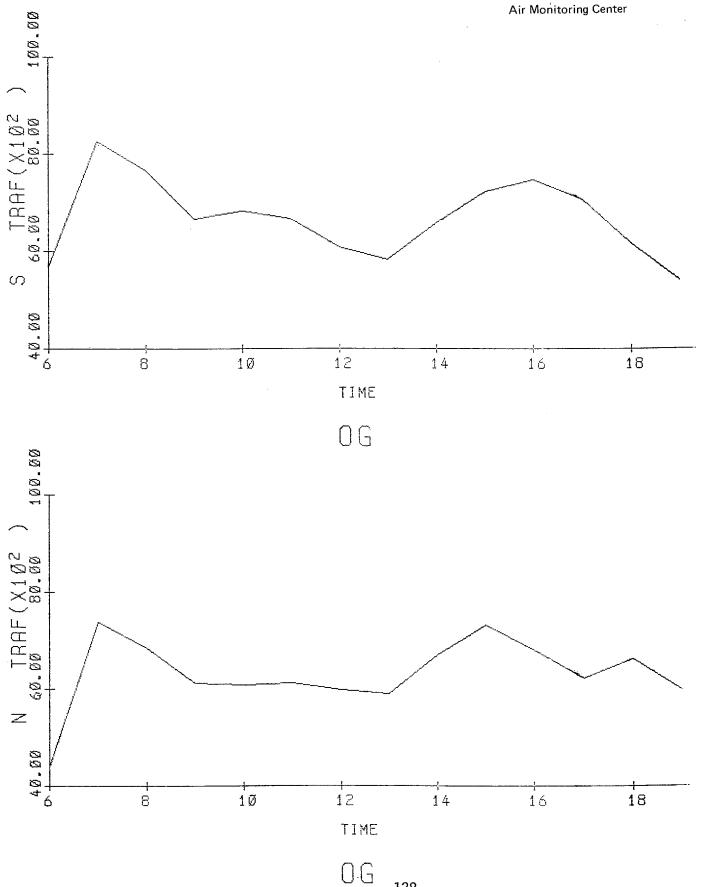




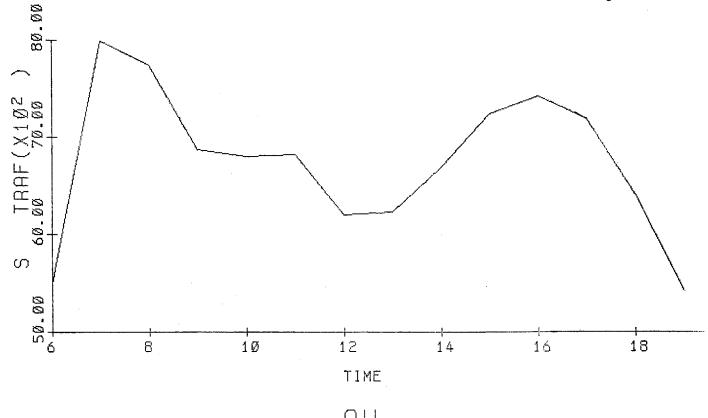
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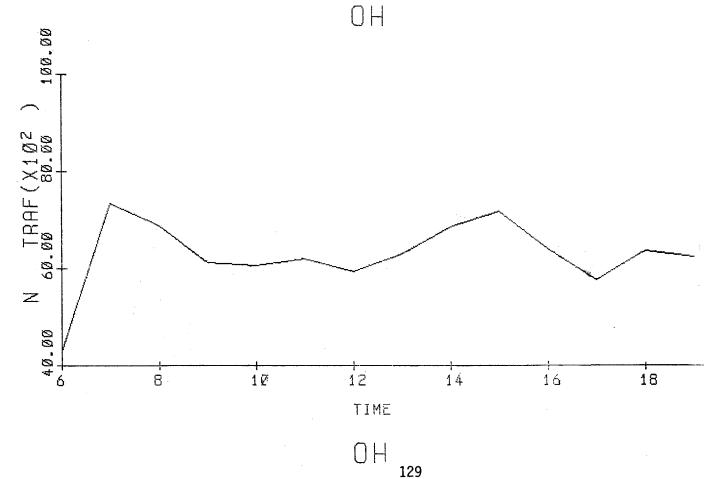


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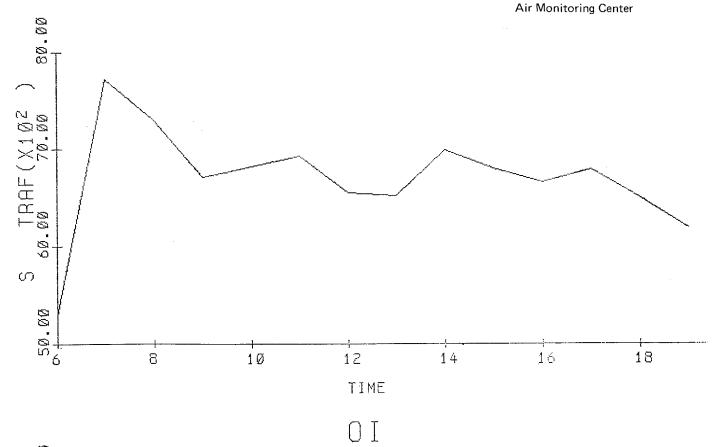


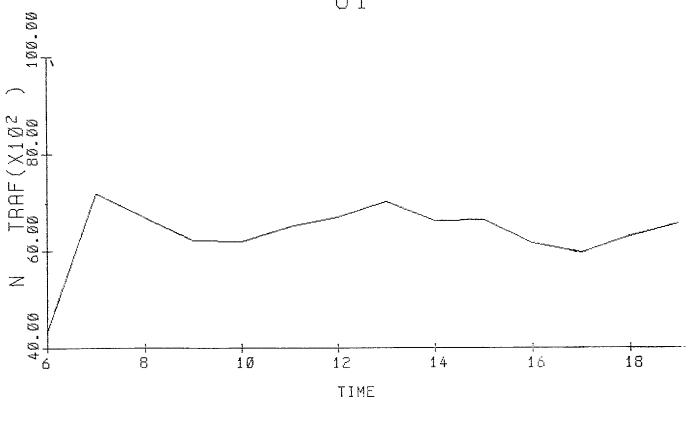


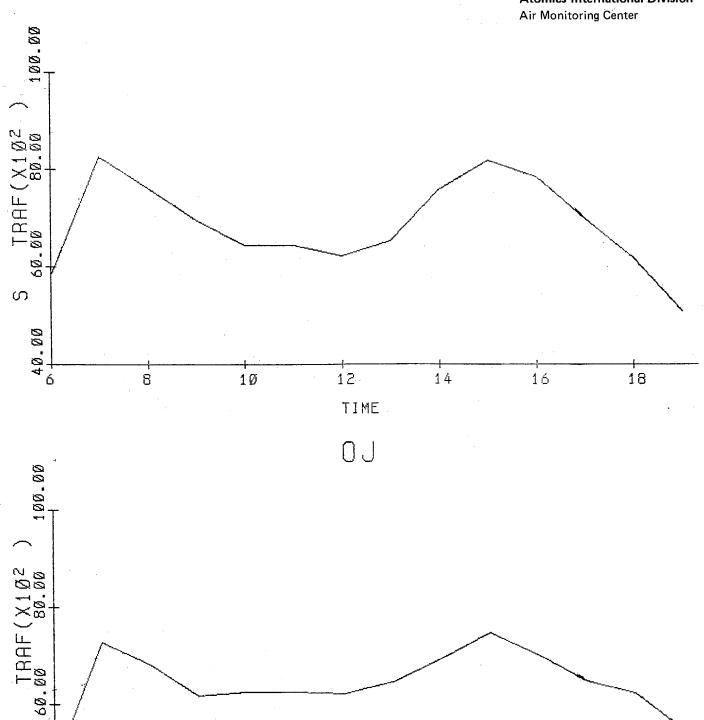












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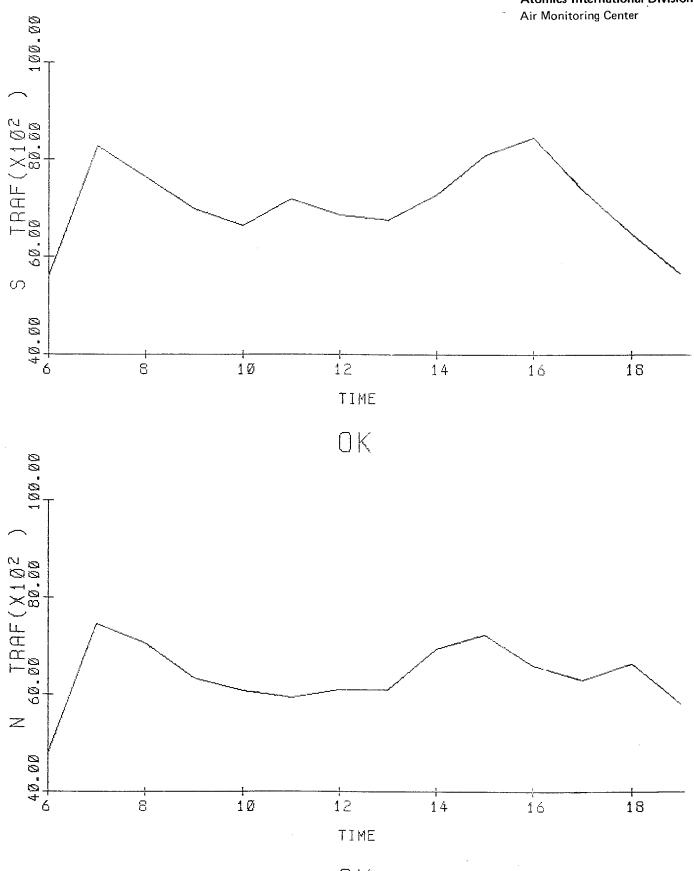
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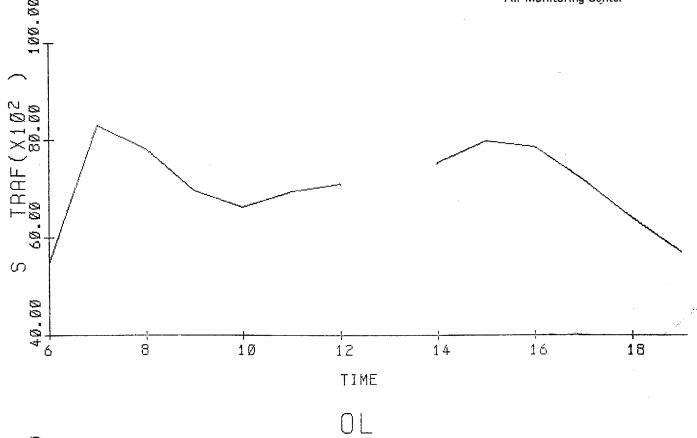
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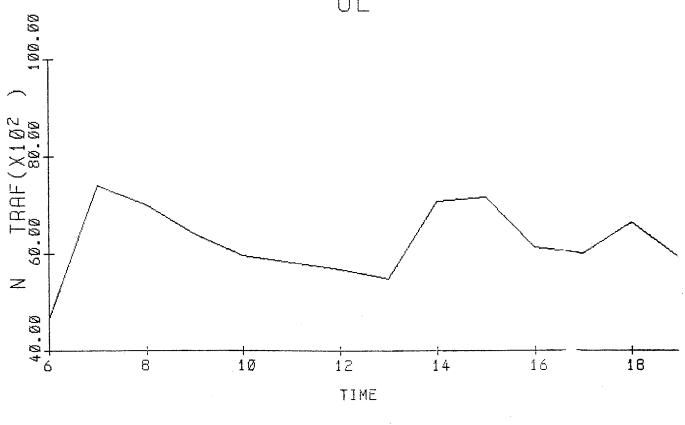
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APPENDIX C

THE REDUCTION OF DATA FROM THE

ELECTRICAL AEROSOL ANALYZER

L. Willard Richards

Presented at the

Aerosol Measurement Workshop University of Florida

March 1976



One of the most useful instruments for determing aerosol size distributions in the 0.01 to 0.5 μm diameter size range is the electrical aerosol analyzer (EAA). The design of the model of the EAA which is currently commercially available has been described by Liu, Whitby, and Pui (1974), and this model has been calibrated with a series of monodisperse aerosols (Liu and Pui, 1975). A data reduction procedure and constants based on this calibration has been recommended by these authors, and will be referred to here as the Liu-Pui data reduction procedure (LPDRP). From the time the LPDRP was available until recent months, most users of the EAA have employed these data reduction constants.

In this article, the same experimental data of Liu and Pui are used to derive a more accurate, but more complicated data reduction procedure, which is referred to here as the revised data reduction procedure (RDRP). It is further shown that the LPDRP and RDRP can give results for the aerosol concentration in some instrument size ranges which differ by a factor of two or three. These differences arise mainly from the assumption in the LPDRP that the signal (current difference) in each instrument channel is proportional to the aerosol concentration in the nominal size range corresponding to that channel. The fact that a monodisperse aerosol can cause an instrument response in two to five different channels shows that this simplification is not always valid. Changes in the concentration of aerosol in the nominal size range of one instrument channel can cause changes in the instrument response in neighboring channels. This effect becomes more important as the aerosol size increases.

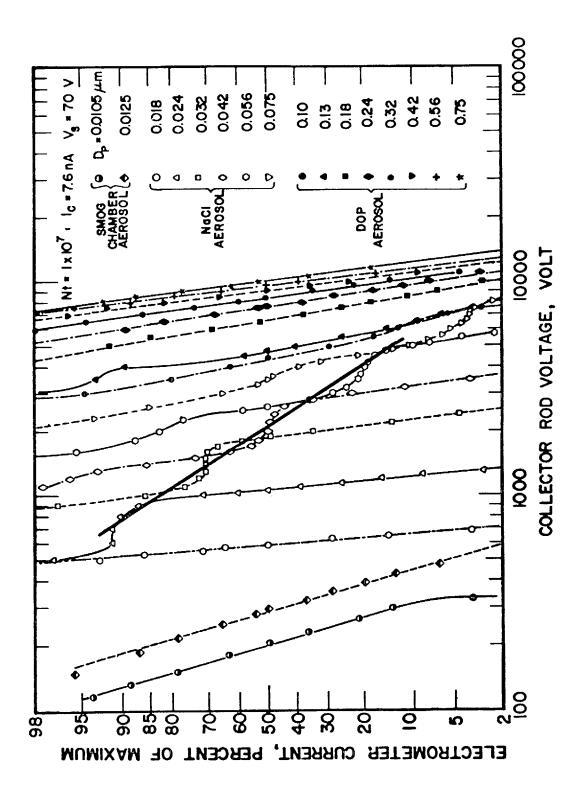
Another factor which causes the apparent instrument calibration constants to vary is that the instrument response to different size aerosols all within the nominal range of one instrument channel can be rather different. In most channels, the instrument sensitivity varies by about a factor of two, so aerosol particles near the large particle boundary of the channel will carry about twice the current at a given concentration compared to particles near the small particle size boundary. These problems can be overcome by using more closely spaced aerosol size increments in the data reduction procedure.



The Liu and Pui calibration data for the EAA were obtained for a geometric progression of sizes of monodisperse aerosols, with a spacing of eight sizes per factor of 10. This spacing is close enough that it is possible to interpolate to estimate rather accurately the response of the instrument to any size of monodisperse aerosol. Since the EAA has a linear response to variations in the aerosol concentration or to combinations of different aerosols, it is possible to calculate the response of the EAA to any aerosol size distribution by representing that distribution by a series of closely space monodisperse aerosols, determining the instrument response to each monodisperse aerosol, then summing these responses. The following text describes how the interpolation was carried out to obtain a closely spaced set of calibration constants, how these constants are used, then some results from their application to experimental data.

Figure 1 shows the calibration data of Liu and Pui (1975) for the aerosol charging conditions of $Nt = 1 \times 10^7$ (ions/cm 3 ((sec). For each size aerosol, as the collector rod voltage increases, the fraction of the aerosol which migrates to the collector rod increases, hence the fraction which passes through the drift tube to the electrometer decreases. As shown in the figure, the smaller aerosols are collected at the lower voltages, and successively larger particles are collected at successively higher voltages. In part, the fact that the aerosol of a given size is collected over a range of voltages is due to the fact that the aerosol is introduced into the drift tube in a zone with a range of distances from the collector rod.

The discrete nature of electrical charge also has an important effect on the shape of the curves. For particles 0.018 μm in diameter and smaller, essentially all particles carry one unit of charge. Slightly larger particles may have either one or two units of charge, and there is a distinct inflection in the curves at the voltage where essentially all of the doubly charged particles have been collected and the singly charged particles pass through uncollected. Triply charged particles begin to show in the data at 0.042 μm



Voltage-current Curves for Charging Conditions with Nt of 1 x 10-(ions/cc)(sec) from Liu and Pui (1975). The Locus of Inflection Points Has Been Added Figure 1.



diameter, and account for 15 or 20% of the electrometer current with 0.056 μm particles. The larger particles carry more units of charge, and the factors which limit the resolution of the instrument smear out the inflections caused by the discrete quantities of charge.

The interpolation between the curves in Figure 1 is made possible by the observation that the shape of the curves near the inflection from one to two units of charge is the same for all curves. In addition, the inflection points are nearly equally spaced on a straight line, which has been added to the figure. For the interpolation, the curves can be translated without rotation in such a way that the inflection point remains on the locus of inflections. The particle size is approximately linearly related to the position of the inflection point on this locus. This procedure permits constructing the calibration curve for any monodisperse particle size between 0.018 μm and 0.75 μm . There is an irregularity in the experimental data at 0.13 μm , which was largely ignored in the interpolations reported below.

In normal operation, the collector rod voltage is advanced stepwise through a series of preset voltages, and the electrometer current read at each voltage. Liu and Pui determined the voltages to be used by:

- 1. Selecting a geometric progression of aerosol sizes with four sizes per factor of 10.
- 2. Determining the collector rod voltage for each size which reduces the electrometer current by half.

The interpolation procedure described above permits constructing a continuous curve for the voltage which reduces the electrometer current by half at each particle size, and this is shown in Figure 2. The points are from the data in Figure 1, and the points which were used to determine the collector rod voltage steps associated with the LPDRP are represented by solid circles.

It can be seen that the transition from one to two units of charge on a particle causes an inflection at 0.042 μm , and from two to three units an inflection at 0.075 μm . As a result, the uniform progression of particle sizes produces a non-uniform progression of voltages. It is interesting to note

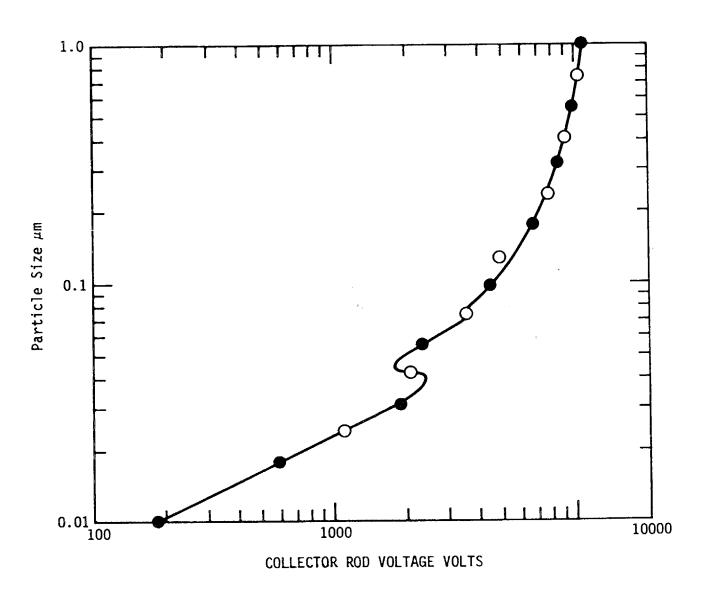


Figure 2. The Collector Rod Voltage for Which the Electrometer Current is Half Its Maximum Values.



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that the voltage progression would have been much more uniform if the particles size progression corresponding to the open circles had been used. If new instrument operating voltages and calibration constants are developed for the LPDRP in the future, the use of a smoothed curve (such as that suggested by the open circles) should be considered.

On first glance at Figure 2, it appears that the EAA responds equally to several different particle sizes near 0.042 μm , in a manner that is similar to the response of optical particle counters to somewhat smaller particles. In fact, examination of Figure 1 shows that no two curves for different size aerosols are alike, so the EAA can always distinguish between monodisperse aerosols of different size.

Liu and Pui (1975) used the curves in Figure 1 to determine the calibration constants for the LPDRP. The same procedure was used with interpolated curves to determine the calibration constants reported in Table 1 for a geometric progression of particle sizes with 24 increments per factor of 10 as given by the equation

$$D_i = 10^{(i-61)/24} \mu m, i = 1,61$$
 (1)

The values of $\mathbf{F}_{i,i}$ in this table are the fraction of the maximum electrometer current due to particles of size i associated with instrument channel j. The fraction of the electrometer current associated with an instrument channel is the difference between the fraction of the current at the two voltages at the channel boundaries as read from the (interpolated) curves in Figure 1.

The calibrations of Liu and Pui (1975) also include the determination for each size aerosol of the instrument sensitivity $\mathbf{S_i}$, i.e., the electrometer current divided by the aerosol concentration at low enough collector rod voltages that the aerosol passes through the drift tube and is collected on the electrometer filter (except for aerosol losses in the instrument, which are largely accounted for by this calibration). The data for aerosol particle sizes between 0.01 μm and 0.03 μm are given in Table 1. For particles smaller than 0.01 μ m, values of S; are given by

| Particle Size Subscript | Particle Diameter D _i | Sensitivity pA 10 ⁶ particles/ | | Fr | actio Each | n of Inst | the E | lectr t Cha | omete nnel | r Cur j | rent | F _{ij} | |
|-------------------------------|--|---|----------|------------|---------------|--------------|------------|----------------|---------------|------------|--------------|-----------------|------------|
| 1 | μm | cm ³ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | >10 |
| 1 2 | 0.0032 0.0035 | 1 | 1. 1. | - | - | _ | - | - | - | - | - | - | - |
| 3 | 0.0038 | (2) | 1. | - | - | - | - | - | - | - | - | - | - |
| 5 5 | 0.0042 | <u> </u> | 1. | - | - | _ | - | - | - | - | - | - | - |
| 6 | 0.0046 0.0051 | Equation | .95 | .05 | - | - | _ | _ | - | _ | - | - | - |
| 7 | 0.0056 | uat | .50 | .50 | - | - | - | - | - | - | - | - | - |
| 8 9 | 0.0062 0.0068 | Eq | .05 | .95 1. | _ | - | _ | - | _ | _ | _ | - | - |
| 10 | 0.0075 | See | + | ī. | - | - | - | - | - | - | - | - | - |
| 11 | 0.0083 | Ĭ | - | 1. | _ | - | - | - | - | - | ~ | - | - |
| 12 13 | 0.0091 0.010 | | <u>-</u> | .95 .50 | .05 .50 | - | <u>-</u> | <u>-</u> | - | _ | _ | - | - |
| 14 | 0.011 | 1.3 | - | - | .95 | - | - | - | - | - | - | - | - |
| 15 16 | 0.012 0.013 | 1.7 2.0 | - | - | 1. | - | - | _ | - | - | - | - | - |
| 17 | 0.013 | 2.4 | - | _ | 1. | - | _ | _ | - | _ | _ | _ | - |
| 18 | 0.016 | 3.0 | - | - | .95 | . 05 | - | - | - | - | - | ~ | - |
| 19 20 | 0.018 0.019 | 3.9 4.8 | - | <u>-</u> | .50 .05 | .50 .95 | _ | - | - | _ | _ | - | - |
| 21 | 0.021 | 5.6 | - | - | .07 | .93 | - | - | - | - | - | - | - |
| 22 23 | 0.025 0.026 | 6.3 7.0 | - | - | .09 - | .91 .97 | .03 | - | | - | - | - | - |
| 23 24 | 0.020 | 8.0 | _ | _ | - | .84 | 16 | _ | _ | _ | _ | _ | - |
| 25 | 0.032 | A | - | - | + | .51 | .49. | | ~ | - | - | - | - |
| 26 27 | 0.035 0.034 | | - | - | - | . 37 | .56 .27 | .07 .29 | - | _ | _ | - | - - |
| 28 | 0.042 | | - | - | _ | .48 | .08 | . 44 | _ | _ | - | - | - |
| 29 30 | 0.046 | Ì | - | - | - | .45 | .16 | .39 .27 | - 06 | - | - | - | - |
| 31 | 0.051 0.056 | | - | - | _ | .20 .14 | .47 .36 | .33 | .06 .17 | _ | _ | _ | _ |
| 32 | 0.062 | | - | - | - | .09 | .20 | .53 | .18 | - | - | - | - |
| 33 34 | 0.068 0.075 | • | _ | - | - | - | .28 .14 | .60 .58 | .09 .24 | .03 | _ | - | - |
| 35 | 0.083 | | _ | _ | - | - | .08 | .69 | .19 | .04 | _ | _ | - |
| 36 | 0.091 | | - | - | - | - | .02 | .58 | .32 | .08 | - | - | - |
| 37 38 | 0.100 0.110 | | - | - | - | _ | _ | .57 .55 | .36 .37 | .07 .08 | - | _ | - |
| 39 | 0.12 | | - | - | - | - | - | . 46 | .46 | .08 | - | - | - |
| 40 41 | 0.13 0.14 | <u></u> | - | - | - | _ | - | .42 .14 | .50 .71 | .08 | - .03 | - | _ |
| 42 | 0.14 | (3) | _ | _ | _ | _ | _ | .10 | .60 | .24 | .06 | _ | - |
| 43 | 0.18 | o | - | - | - | - | - | .03 | .47 | .39 | . 08 | .03 | - |
| 44 45 | 0.195 0.21 | Equati | - | - | _ | _ | - | _ | .40 .31 | .42 .46 | .13 | . 05 . 05 | - .02 |
| 46 | 0.24 | Equ | - | - | - | - | - | - | .22 | . 48 | .21 | . 06 | .03 |
| 47 48 | 0.26 0.29 | ∱See | - | - | - | - | - | - | .17 .11 | .50 .48 | .23 .27 | .07 .09 | .03 .05 |
| 49 | 0.32 | Š. | _ | _ | _ | _ | _ | _ | .08 | .42 | . 32 | . 11 | . 07 |
| 50 | 0.35 | | - | - | - | - | - | - | . 05 | .40 | .35 | .12 | .08 |
| 51 52 | 0.38 0.42 | | - | - | _ | _ | - | - | .03 | .34 | .36 .36 | .15 .21 | .12 .13 |
| 53 | 0.46 | | - | - | - | - | - | - | - | .26 | .37 | .20 | . 17 |
| 54 55 | 0.51 | | - | - | - | - | - | - | - | .22 .18 | .35 .36 | .24 .25 | .19 .21 |
| 56 | 0.56 0.62 | | _ | - | _ | _ | - | _ | <u>-</u> | .14 | .35 | .25 | .26 |
| 57 | 0.68 | | - | - | - | - | - | - | - | .13 | .31 | .25 | .31 |
| 58 59 | 0.75 0.83 | | - | - | - | - | - | - | - | .12 | . 29 . 25 | .24 .24 | .35 .43 |
| 60 | 0.91 | | - | - | _ | _ | - | - | - | .08 | .20 | .24 | .48 |
| 61 | 1.00 | * | - | - | - | - | - | - | - | .07 | .15 | . 26 | .52 |

$$\log_{10} S_i = 13.975 + 7.033 \log_{10} D_i$$
 , (2)

and for particles larger than 0.03 μm by

$$\log_{10} S_i = 2.618 + 1.113 \log_{10} D_i$$
 (3)

where S is in units of pA per 10^6 particles/cm and D is in units of μm .

In a hypothetical case in which a number concentration N_i particles/cm 3 of each size D_i is supplied to the EAA, the observed current difference for each instrument channel would be

$$\Delta I_{j} = \sum_{i=1}^{61} N_{i} S_{i} F_{ij} \times 10^{-6} . \tag{4}$$

The factor of 10^{-6} arises because S_i is given in units of pA per 10^6 particles/ cm^3 .

The particle size distribution which most nearly gives the same instrument response as an observed response can be found by:

- 1. Adopting a criterion for goodness of fit, so various fits can be ranked in order of decreasing quality,
- 2. Assuming a trial size distribution N_i ,
- Calculating the instrument response from Equation (4),
- 4. Determining the goodness of fit,
- 5. Adjusting the trial size distribution so as to improve the fit, and
- Continuing with steps 3 through 5 until the goodness of fit parameter is minimized.

In the work reported below, the problems at hand were adequately solved by using a visual observation of a plot of the data in step 1, and having the computer operator choose new parameters in step 5. However, it should be straightforward to automate the entire procedure.

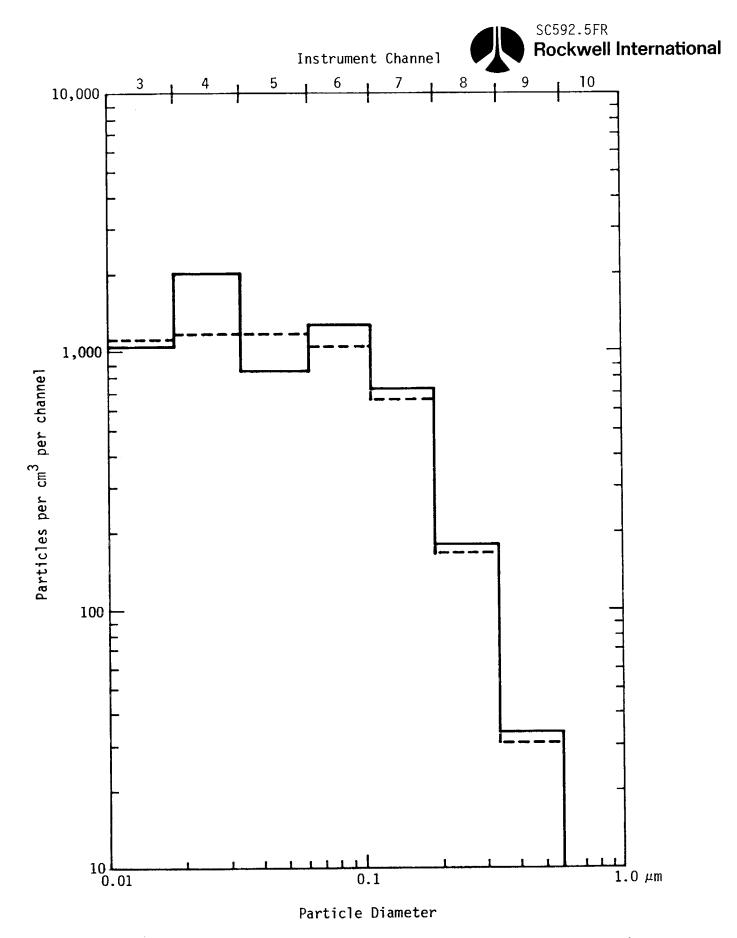


Figure 3. Number Concentration of a Flow-Reactor Produced Aerosol Measured with Nt = 1×10^7 cm⁻³ sec. The Solid Line Contains Results from the LPDRP and the Dotted Line from the RDRP.



The above procedure is simplified if some functional form is assumed for the size distribution. For atmospheric aerosols, three size classes appear to be important, and the experimental data are usually adequately represented by a trimodal log-normal distribution. Only two of the aerosol size classes fall within the range of the EAA, so a bimodal log-normal distribution is usually the mathematical form of choice in reducing EAA data for atmospheric aerosols, and many aerosols from other sources.

To represent a log-normal distribution containing a concentration of $N_{\sf t}$ particles/cm 3 by a series of monodisperse aerosols of the sizes given by Equation (1), the concentration of each size $N_{\sf i}$ is given by the relation

$$N_i = N_t \frac{(\ln 10)/24}{\sqrt{2\pi} \sigma} \exp{-\frac{(\ln D_i - \ln D_g)}{2\sigma^2}},$$
 (5)

where $\rm D_g$ is the geometric mean diameter and σ is the standard deviation. A bimodel log-normal distribution can be represented by the sum of two such relations. Therefore, there are six adjustable parameters for a bimodal log-normal distribution, $\rm N_t$, $\rm D_q$ and σ for each mode.

The first example of the use of this procedure shows data for an aerosol obtained from a flow reactor (Lipeles, 1976). In this case, a functional form closely approximating the aerosol size distribution was chosen, and the instrument response to this size distribution was calculated. Then, this calculated instrument response was used to determine new calibration constants for the LPDRP, and the data given by the dotted line sigments in Figure 3 were obtained. The solid line segments show the results obtained by the LPDRP. The results in this figure were the first obtained by the methods presented here, and encouraged the further use of this method.

Another result is shown in Figure 4. These data were obtained immediately downwind from a major freeway in Los Angeles. (The EAA was operated with charging conditions of Nt = 7×10^6 (ions/cm 3)(sec), so calibration constants derived for this charging condition were used in the reduction of these data). The points representing the experimental data were obtained from the observed instrument response using the LPDRP. The curve represents the best-fit bimodal log-normal distribution, and is made up of straight line segments joining the

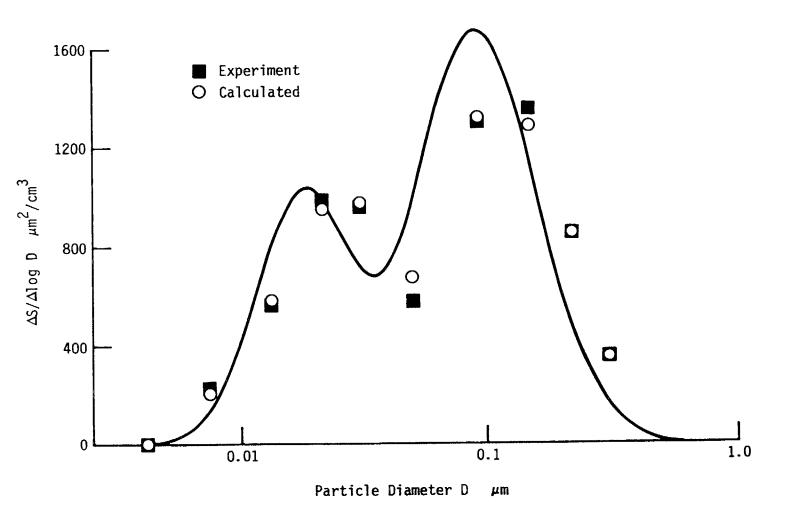


Figure 4. Particle Size Distribution Data Obtained Near a Freeway with Nt = 7×10^6 (ions/cm³)(sec).



values of N_{i} when presented in this aerosol surface vs aerosol size representation. The points representing the calculated instrument response were obtained from the current differences calculated for each instrument channel from the N_{i} represented in the curve. The LPDRP was used to convert the calculated instrument response into the points in the figure. When the calculated and observed points in the figure are equal, the calculated and observed instrument current differences are equal. Thus, the transformation used for the observed and calculated points in Figure 4 is one way of weighting the differences between the observations and calculations when searching for the best fit.

In the fitting procedure, values of D_g and σ for each mode were selected by hand, and the values of N_t for each mode were selected to obtain the best least-squares fit of the data points as represented in Figure 4. Thus, the data were transformed to the $\Delta S/\Delta \log d$ representation before the sum of the square of the errors was determined. Needless to say, the choice of a goodness of fit criterion was arbitrary, and other choices could have been used.

The results in Figure 4 show that it was possible to obtain close agreement between the observed and calculated instrument response, (hence the criterion used to determine the best fit is not of great importance). The quality of this fit is not strong evidence for the bimodal log-normal nature of aerosol distributions, because six parameters were adjusted in the fit to nine non-zero data points. The best evidence for the bimodal nature of the aerosol was the observation that the smaller particle size mode (nuclei mode) was directly due to the freeway traffic, and the larger particle size mode (accumulation mode) was not importantly influenced by the traffic. However, the quality of the fit does show that the bimodal log-normal distribution is adequate to represent the data.

It is apparent that there is some difference between the results obtained by the LPDRP (shown by the points) and the RDRP (shown by the curve). For one thing, the values of $\mathbf{D}_{\mathbf{g}}$ for each mode from the RDRP are smaller than from the LPDRP.

Table 2

RATIOS OF CALIBRATION CONSTANTS

 $Nt = 1 \times 10^7 \text{ ions cm}^{-3} \text{ sec}$

(Liu, Pui Constants/Constants Calculated Here)

Assumed Size Distributions

| | Accumulation Mode | | | Nuclei Mode | | |
|---------|----------------------|-----|---|----------------|------------------------------|------|
| | D _g | σ | | | $^{\mathrm{D}}\mathrm{_{g}}$ | σ |
| Number | 0.061 | 0.6 | 7 | | 0.013 | 0.42 |
| Surface | 0.150 | | | | 0.018 | |
| Volume | 0.235 | | | | 0.022 | |

| Instrument Channel | Nominal Aerosol Size m | Ratios of Calibr | ration Constants |
|-----------------------|------------------------------|------------------|------------------|
| 2 | 0.0075 | 3.85 | 3.04 |
| 3 | 0.0133 | 1.36 | 0.90 |
| 4 | 0.0237 | 3.10 | 0.94 |
| 5 | 0.0422 | 0.80 | 0.66 |
| 6 | 0.0750 | 1.28 | (6.70) |
| 7 | 0.133 | 1.04 | |
| 8 | 0.237 | 0.96 | Too |
| 9 | 0.422 | 1.36 | Few |
| 10 | 0.750 | 3.70 | Particles |



Another comparison between the two data reduction procedures is shown in Table 2. Two different log-normal aerosol size distributions were assumed, one appropriate for accumulation mode aerosols and the other for nuclei mode aerosols. The instrument response for an arbitrary concentration of each aerosol was calculated. Then the concentration of aerosol particles within the size range of each nominal instrument channel specified by the LPDRP was divided by the calculated current difference for that channel to obtain calculated values for the instrument calibration constants. The calibration constants reported by Liu and Pui were then divided by the calculated constants to obtain the ratios given in Table 2.

The data for channels 7 and larger for nuclei mode aerosols are not reported for two reasons:

- In this size range, the nuclei mode aerosol concentration falls off extremely rapidly with increasing particle size, with the result that the calculated calibration constants are orders of magnitude larger than those of the LPDRP, and
- 2. There is no practical use for the calculated constants because no actual aerosol would fall off as rapidly in concentration in this size range as does the assumed size distribution.

The data for channel 6 are enclosed in parentheses because the above comments are partly relevant to this result.

There are two important things to note in Table 2. The first is that the calibration constants calculated here for the accumulation mode and nuclei mode size distributions are as much as a factor of three different from those recommended for use in the LPDRP. The second is that the calibration constants calculated here depend on the aerosol size distribution. This is especially notable in instrument channel 4 for the size distributions in Table 2, but such differences can occur in other instrument channels for other size distribution.

In summary, it is believed that the existing data reduction procedures for the EAA contain approximations which have a significant effect on the derived results, but that more elaborate data reduction procedures are easily derived which remove these problems, and allow experimentalists to obtain data from



the EAA which exploit its full potential. It should be possible to make computer routines generally available to provide easy access to these data reduction procedures.

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APPENDIX D

ADDITIONAL MONITORING FOR SULFURIC ACID



When the editing of the data bank was completed and the two-hour average differences and normalized differences were calculated and tabulated, it became apparent that the data contained the uncertainties described in Sections 6.0 and 7.0 of this report. Therefore, it was decided to devote less effort to the interpretation of these data than had been planned.

It was recommended to the ARB that about \$5,000 of the remaining funding be directed to measurements of sulfuric acid near a freeway, and this recommendation was accepted. The work toward that goal is reported in this Appendix.

In summary, a low-temperature volatilization method for sulfuric acid which was under development at the AMC was calibrated, and the measurement method was evaluated in the ambient air in Newbury Park, California. Signals corresponding to roughly 1 μ g/m³ sulfuric acid were observed. Since these "background" signals were comparable to or larger than the signals to be expected near a freeway, they greatly increased the difficulty of measuring sulfuric acid concentrations due to catalyst equipped automobiles, and the attempt to make these measurements was discontinued. The following, more detailed, account of this work concludes with a short summary of the best current information on the cause of these signals, which are like those from sulfuric acid.

The measurement method used in this work was first described by L. W. Richards in a proposal to the EPA, and after work on its development was begun, it was described at an American Chemical Society Meeting (Richards, 1973). The measurement method has been reduced to practice in an instrument delivered to the EPA (Mudgett, Richards, and Roehrig, 1974a, 1974b), and has been patented (Richards and Mudgett, 1974). The instrument was operated by the EPA during the General Motors Sulfate Dispersion Experiment (Stevens, et al., 1976), and determined amounts of sulfuric acid in the range between 0.7 and $5.1~\mu g/m^3$.

The measurement method uses a two-step procedure. In the first step, ambient air is passed through a Teflon filter to collect the sulfuric acid and other particulates which might be present. In the second step, the sulfuric acid is volatilized from the filter by dry, warm air and transported to a Meloy SA 160-2 Flame Photometric Detector Sulfur Gas Analyzer (FPD). This procedure



differs from previous work by placing emphasis on the use of dryness to separate sulfuric acid from other sulfur containing particulates. It has also been found that a small amount of methanol in the dry air flow can improve the efficiency of the volatilization of the sulfuric acid and its transport to the FPD. The monitor has been designed to allow considerable flexibility in the monitoring cycle time and in the flow rate of the sample air. The analytical procedure detects only sulfur containing compounds which are in the particulate phase under ambient conditions and become volatilized when dried and warmed in the presence of methanol. At the time the work reported here was begun, it was believed that this procedure was free from significant interferences, except those which occur when the sulfuric acid reacts with other components of the aerosol on the filter.

Any method for detecting sulfuric acid is subject to interferences from basic materials present in the atmosphere. Even a neutral material such as sodium chloride from sea salt can interfere, by converting sulfuric acid into sodium sulfate and gaseous HCl. Therefore, precautions must be taken to minimize and quantify these interferences. In addition, it is possible that other volatile sulfates can interfere in the procedure just described. Repeated experiments have shown that ammonium sulfate does not give a positive interference, even when tens of micrograms are deposited on the filter as a submicron sized aerosol, provided the volatilization temperature is kept below about 180°C. On the other hand, ammonium sulfate on the filter can cause a negative interference by reacting with sulfuric acid to form ammonium bisulfate, which is not detected, provided the volatilization temperature is low enough.

In 1974 and 1975, an improved model of the sulfuric acid monitor was constructed at the AMC. At the time the work reported here was proposed, the calibration of the instrument was underway. Under this ARB contract, the Berglund-Liu vibrating orifice aerosol generator (Berglund and Liu, 1973) was used to generate monodisperse aerosols of a few microns diameter of known composition. Calibration experiments confirmed that the low temperature volatilization technique does not respond to ammonium sulfate at the volatilization temperatures in use. In addition, the metal sulfates are even less volatile, and also give no signals. There was not enough time during this ARB funded work to completely characterize the response of the instrument to ammonium bisulfate, but later

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